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Utah Water Research Lab., Logan

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WASTE/SOIL TREATABILITY STUDIES FOR FOUR COMPLEX INDUSTRIAL WASTES: METHODOLOGIES AND RESULTS

Volume 1

Literature Assessment, Waste/Soil Characterization, Loading Rate Selection

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16. ABSTRACT

This two-volume report presents information pertaining to quantitative evaluation of the soil treatment potential resulting from waste-soil interaction studies for four specific wastes listed under Section 3001 of the Resource Conservation and Recovery Act (RCRA). Volume 1 contains information from literature assessment, waste-soil characterization, and treatability screening studies for each selected waste. Volume 2 contains results from bench-scale waste-soil interaction studies; degradation, transformation, and immobilization data are presented for four specific wastes: API separator sludge, slop oil emulsion solids, pentachlorophenol wood preserving waste, and creosote wood preserving waste. The scope of the study involved assessment of the potential for treatment of these hazardous wastes using soil as the treatment medium.

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NOTICE

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

When applicable, enviromentally acceptable treatment of hazardous waste in soil systems is a function of operation and management practices at a given site. Successful operation and management practices are dependent on identifying waste loading constraints for that particular site. There is currently a lack of readily available information relative to impact of waste loading rates and frequencies on transformation and transport of hazardous organic constituents in waste-soil matrices and to methodologies for making such determinations. This two-volume report is intended to propose one set of methodologies for determining waste loading constraints for soil systems and to provide an assessment of data collected using the proposed set of methodologies for two petroleum refining and two wood preserving waste streams applied to two soil types. Volume 1 contains results from literature assessment, waste/soil characterization and treatability screening studies; Volume 2 contains results from bench-scale degradation, transformation and immobilization studies.

Clinton W Hall

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ABSTRACT

This is Volume 1 of a two-volume report that presents information pertaining to quantitative evaluation of the soil treatment potential resulting from waste-soil interaction studies for four wastes listed under Section 3001 of the Resource Conservation and Recovery Act (RCRA). This volume contains information from literature assessment, waste-soil characterization, and treatability screening studies for loading rate selection for each waste. The four wastes included API separator sludge, slop oil emulsion solids, pentachlorophenol wood preserving waste, and creosote wood preserving waste. Chemical analyses and bioassays were used to characterize wastes, soils, and waste-soil interactions.

Objectives of the research reported in this volume were to:

(1) Conduct a literature assessment for each waste to obtain specific information pertaining to soil treatment (degradation, transformation, and immobilization) of hazardous constituents identified in each waste.

(2) Chemically characterize wastes for specific constituents of concern; and characterize two experimental soils for assessment of specific parameters that influence soil treatability.

(3) Conduct laboratory screening experiments using a battery of bioassays to determine waste loading rates (mg waste/kg soil) to be used in subsequent longer term experiments designed to assess potential for treatment of each selected waste in soil.

Specific results and conclusions based on the objectives include:

(1) Literature assessment of specific hazardous constituents in each waste indicated a potential for treatment in soil systems.

(2) Chemical characterization of the wastes by GC/MS, GC, and HPLC identified the PAH class of semivolatile constituents as common to each waste. In addition, the PCP wood preserving waste contained pentachlorophenol and some dibenzo-p-dioxins and dibenzofurans; however, no tetrachlorodibenzodioxins were detected at the detection limit of 10 ppb.

(3) A comparative study of the sensitivity of five microbial assays for selection of initial waste loading rates indicated that Microtox, soil dehydrogenase, and soil nitrification assays correlated well and were the most sensitive to the presence of hazardous wastes, and would result in selecting lower soil loading rates. Soil respiration and viable soil microorganism plate counts were highly

variable and less sensitive, and would result in selecting higher loading rates.

(4) Based on screening results using the Microtox assay, initial loading rates for petroleum refinery wastes (6 to 12 percent) were indicated to be an order to magnitude higher than for wood preserving wastes (0.1 to 1.3 percent).

(5) Loading rates selected for the clay loam soil were generally higher than rates selected for the sandy loam soil, thus indicating a difference with respect to the effect of soil type on waste-soil interactions.

Based on results obtained for the specific wastes and soils evaluated, the use of chemical analyses alone appears to be insufficient to characterize waste-soil interactions and the effects of waste-soil mixtures on microbial activity. Chemical and bioassay characterization of waste, soil, and waste-soil mixtures provides valuable information concerning treatment potential for industrial wastes.

CONTENTS

Notice ii
Foreword iii
Abstract iv
Figures vii
Tables x
Acknowledgments xiii

1. Introduction 1
    Objectives 2
    Evaluation Approach 2
    Waste Characterization 4
    Soil Characterization 4
    Waste Loading Rate Determination 4
    Waste Treatment in Soil 5
    Mathematical Model for Soil-Waste Processes 5
2. Conclusions 7
3. Recommendations 8
4. Literature Review 9
    Introduction 9
    Wood Preserving Industry 10
    Petroleum Refining Industry 42
5. Results and Discussion 56
    Quality Assurance/Quality Control 56
    Waste Characterization 57
    Soil Characterization 97
    Waste Loading Rate Evaluation 106

References 142

FIGURES

Number Page

1. Rates of degradation of PAH compounds in soil as a function of initial soil concentrations (Overcash and Pal 1979) 31

2. Biodegradation of PCP 38

3. Scheme for the analysis of waste samples for organic constituents. 62

4. Schematic of the Ames assay 65

5. Ames assay results for creosote sludge base/neutral fraction . . 94

6. Ames assay results for pentachlorophenol sludge base/neutral fraction 95

7. Ames assay results for pentachlorophenol sludge acid fraction . . 96

8. Ames assay results for API separator sludge base/neutral fraction. 98

9. Ames assay results for slop oil emulsion solids base/neutral fraction 99

10. Soil moisture characteristic curve for Durant clay loam 105

11. Soil moisture characteristic curve for Kidman sand loam 105

12. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant clay loam soil for loading rate determination, Trial #1 119

13. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant clay loam soil for loading rate determination, Trial #2 119

14. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant clay loam soil for loading rate determination, Trial #3 120

15. Soil respiration results for creosote waste mixed with Durant clay loam soil 121

FIGURES (CONTINUED)

Number Page

16. Toxicity of water soluble fraction measured by the Microtox assay for creosote waste mixed with Kidman sand loam soil for loading rate determination 122

17. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for PCP wood preserving waste mixed with Durant clay loam soil for loading rate determination 122

18. Soil respiration results for PCP waste mixed with Durant clay clay loam soil 123

19. Toxicity of water soluble fraction measured by the Microtox assay for PCP wood preserving waste mixed with Kidman sandy loam soil for loading rate determination 125

20. Toxicity of water soluble fraction measured by the Microtox assay for API separator sludge waste mixed with Durant clay loam soil for loading rate determination 125

21. Soil respiration results for API separator sludge mixed with Durant clay loam soil 126

22. Toxicity of waste soluble fraction measured by the Microtox assay for API separator sludge waste mixed with Kidman sandy loam soil for loading rate determination 127

23. Toxicity of water soluble fraction measured by the Microtox assay for slop oil waste mixed with Durant clay loam soil for loading rate determination 127

24. Soil respiration results for slop oil emulsion solids mixed with Durant clay loam soil 129

25. Toxicity of water soluble fraction measured by the Microtox assay for slop oil waste mixed with Kidman sandy loam soil for loading rate determination 130

26. Microtox response to PCP waste application to Kidman soil after 24±2 h incubation (LSD=least significant difference) 132

27. Initial ammonium and nitrite ion oxidation in response to treatment of Kidman soil with PCP waste after 24±2 h incubation (LSD=least significant difference) 133

28. Dehydrogenase response to PCP application to Kidman soil after 24±2 h incubation (LSD=least significant difference) 134

FIGURES (CONTINUED)

Number Page

29. Respiration response to application of PCP waste to Kidman soil after 24±2 h incubation (LSD=least significant difference) . 135

30. Viable aerobic heterotrophic bacteria and fungal propagules in Kidman soil treated with PCP waste after 24±2 h incubation (LSD=least significant difference) 136

31. Microtox response to slop oil emulsion solids waste application to Kidman soil (LSD=least significant difference) 138

32. Initial ammonium and nitrite ion oxidation in response to treatment application of slop oil emulsion solids to Kidman soil (LSD=least significant difference) 139

33. Dehydrogenase response to slop oil emulsion solids waste application to Kidman soil (LSD=least significant difference) 140

TABLES

Number Page

1. Principal constituents of high-temperature creosote (Winslow 1973) 11
2. Specific components in creosote oil (Lorenz and Gjovik 1972) . . 12
3. Selected physical properties of PCP (Crosby 1981) 13
4. Ring arrangement and relative stability of PAH compounds (Blumer 1976) 15
5. Properties of 16 priority pollutant PAH compounds 16
6. Summary of physical properties for selected phenolic compounds (Versar Inc. 1979) 19
7. Health effects of chemical constituents of creosote (U.S. EPA 1984a) 20
8. Human health effects of exposure to creosote (U.S. EPA 1974) . . 23
9. Polynuclear azaarenes in creosote-PCP wood preservation wastewater (Adams and Glam 1984) 24
10. Kinetic parameters describing rates of degradation of PAH and phenolic compounds in soil systems (Sims and Overcash 1983, ERT 1985b) 28
11. Summary of soil sorption data for constituents of creosote waste (ERT, Inc. 1985b) 34
12. Summary of bench and pilot scale PCP degradation studies (ERT, Inc. 1985a) 40
13. Refinery wastes known to be land treated and relative percentages of each waste which are land treatment (ERT 1984) 43
14. Physical composition of refinery wastes (Engineering Science 1976) 44
15. Composition of 12 API refinery wastes (Overcash and Pal 1979) . . 44

TABLES (CONTINUED)

Number Page

16. Categories for Appendix VIII constituents in refinery wastes which are land treatment (ERT, Inc. 1984) 45

17. Constituents of petroleum wastes (as approved by U.S. EPA) . . . 46

18. Waste characterization for aggregate of sixteen solid waste streams from a category IV petroleum refinery (Pal and Overcash 1980) 50

19. Relative resistance of hydrocarbons to biological oxidation (Fredericks 1966) 51

20. Results of degradation of petroleum wastes at a land-farm after 25 months (Meyers and Huddleston 1979) 53

21. Waste characterization parameters 57

22. Hazardous wastes selected for evaluation 58

23. GC/MS analysis conditions 64

24. Physical characterization of wastes 68

25. Characterization of residues in hazardous wastes 69

26. Characterization of metals in petroleum refinery wastes 70

27. Characterization of metals in wood preserving wastes 71

28. Characterization of metals in petroleum refinery wastes: quality control data 72

29. Characterization of metals in creosote wastes: quality control data for spiked creosote waste samples - high and low level . . . 73

30. Characterization of metals in pentachlorophenol wastes: quality control data for spiked pentachlorophenol waste samples - high and low level 74

31. Characterization of metals in creosote and pentachlorophenol wastes: quality control data for EPA quality control samples . . 75

32. Total organic carbon (TOC) content of hazardous waste samples . . 76

33. Characterization of oil and grease in hazardous waste samples . . 76

TABLE (CONTINUED)

Number	Page
34. Organic compounds tentatively identified in API separator sludge waste (base/neutral fraction) by GC/MS	77
35. Organic compounds tentatively identified in slop oil emulsion waste (base/neutral fraction) by GC/MS	80
36. Organic compounds tentatively identified in creosote waste (base/neutral fraction) by GC/MS	84
37. Organic compounds tentatively identified in pentachlorophenol waste (base/neutral fraction) by GC/MS	85
38. Organic compounds tentatively identified in creosote waste and pentachlorophenol waste (acid fraction) by GC/MS	88
39. Organic compounds tentatively identified in API separator sludge and slop oil waste samples (volatile fraction) by GC/MS	90
40. Organic compounds tentatively identified in PCP and creosote waste samples (volatile fraction) by GC/MS	91
41. Concentration of individual PAH compounds in wastes determined by HPLC	92
42. Chlorinated dibenzo-p-dioxins and dibenzofurans in pentachlorophenol waste by GC/MS	93
43. Toxicity of water soluble fraction measured by the Microtox assay for hazardous waste samples	93
44. Soil physical and chemical properties evaluated for soil characterization	100
45. Measurement methods and data quality objectives for soil analyses	101
46. Characterization of Durant clay loam soil collected from hazardous waste land treatment facility, U.S. EPA, Ada, Oklahoma	103
47. Characterization of Kidman sandy loam soil collected from USU Agricultural Experiment Farm at Kaysville, Utah	104
48. Soil loading rates for wastes based on Microtox and soil respiration results	131

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SECTION 1

INTRODUCTION

Land treatment is the hazardous waste management technology pertaining to application/incorporation of waste into the upper layers of the soil for the purpose of degrading, transforming, and/or immobilizing hazardous constituents contained in the applied waste (40 CFR Part 264). Land application systems have been utilized for a variety of industrial wastes; however, application of hazardous industrial waste utilizing a controlled engineering design and management approach has not been widely practices. This is due, in part, to the lack of a comprehensive technical information base concerning the behavior of hazardous constituents as specifically related to current regulatory requirements (40 CFR Part 264) concerning treatability in soil, i.e., degradation, transformation, and immobilization of such constituents. Soil treatment systems that are designed and managed based on a knowledge of soil-waste interactions may represent a significant technology for simultaneous treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner.

In this research project, representative hazardous wastes from two industrial categories, wood preserving and petroleum refining, were evaluated for potential for treatment in soil systems. A literature assessment for each waste category was conducted as an aid in the prediction of land treatment potential. The literature assessment also was used as a guide to design an experimental approach to obtain specific treatability information pertaining to degradation, transformation, and immobilization of hazardous constituents in soil.

Results of this research project are contained in two volumes. The two volumes contain information concerning an approach (methodology) and results for evaluating the potential for treatment of hazardous waste in soil systems.Volume 1 contains information concerning literature review, results of laboratory waste and soil characterization, bioassay results for soil microbial activity in the presence of hazardous wastes, and experimental approaches and results for selection of waste loading rates using a bioassay battery. Volume 2 contains information concerning results of treatability studies designed to generate degradation, transformation, and immobilization information for API separator sludge, slop oil emulsion solids, pentachlorophenol wood preserving waste, and creosote wood preserving waste.

OBJECTIVES

Specific objectives of this research project were to:

(1) Conduct a literature assessment for each candidate hazardous waste, API separator sludge, slop oil emulsion solids, creosote wood preserving waste, and pentachlorophenol (PCP) wood preserving waste to obtain specific land treatability information, i.e., degradation, transformation, and immobilization, for hazardous constituents identified in each waste.

(2) Characterize candidate wastes for identification of specific constituents of concern; and characterize experimental soils for assessment of specific parameters that influence land treatability potential.

(3) Conduct treatability screening experiments using a battery of microbial assays to determine waste loading rates (mg waste/kg soil) to be used in subsequent experiments to assess potential for treatment.

(4) Develop degradation, transformation, and immobilization information as a function of loading for each candidate hazardous waste in the soil types.

(5) Develop methodologies for the measurement of "volatilization-corrected" degradation rates and for measurement of partition coefficients; use methodologies developed to generate degradation kinetics/partition coefficients for a subset of soil/waste combinations and for constituents common to all candidate wastes.

Information generated relative to the first three objectives is presented in this volume (Volume 1) of the project report.

EVALUATION APPROACH

Standards are promulgated in 40 CFR Part 264.272 for demonstrating land treatment of hazardous wastes. The standards require demonstration of degradation, transformation, and/or immobilization of a candidate waste in the treatment soil. Demonstration of degradation of waste and waste constituents is based on the loss of parent compounds within the soil/waste matrix. Complete degradation is the term used to describe the process whereby waste constituents are mineralized to inorganic end products, generally including carbon dioxide, water, and inorganic species of nitrogen, phosphorus, and sulfur. The rate of degradation may be established by measuring the loss of parent compound from the soil/waste matrix with time. Transformation refers to the partial degradation in the soil converting a substance into an innocuous or harmless form, or problem wastes into environmentally safe forms (Huddleston et al. 1986). Ward et al. (1986) also discussed the difference between rates of mineralization (for complete degradation) and rates of biotransformation. Therefore transformation refers to the formation of intermediates during the process of degradation or the formation of intermediates as refractory compounds in the soil matrix. Immobilization refers to the extent of retardation of the downward transport, or leaching potential, and upward transport, or volatilization potential, of waste constituents. The mobility potential for waste constituents to transport from the waste to water, air, and soil phases is affected by the relative affinity of the waste constituents for each phase, and can be characterized in column and batch reactors. Therefore, demonstration of soil treatment requires an evaluation of degradation, transformation, and immobilization processes, and the quantification of the processes for obtaining an integrated assessment of the design and management requirements for successful assimilation of a waste in a soil system.

The requirement for demonstrating treatment, i.e., degradation, transformation, and/or immobilization, can be addressed using several approaches. Information can be obtained from several sources, including literature data, field tests, laboratory analyses and studies, theoretical parameter estimation methods, or, in the case of existing land treatment units, operating data. Information presented in Literature Review in this report addresses information obtained from literature data and existing land treatment units. Specific information obtained from literature sources included quantitative degradation, transformation, and immobilization information for waste-specific hazardous constituents in soil systems. Four hazardous wastes are considered, including API separator sludge, slop oil emulsion solids, creosote sludge and pentachlorophenol sludge. However, the U.S. EPA considers the use of only literature information as insufficient to support demonstration of land treatment of hazardous wastes at the present time. A laboratory experimental approach used during this project for obtaining additional information concerning treatability data for the four hazardous wastes selected for study is presented. Results using the approach are also presented.

The regulations also require that the effect of design and management practices on soil treatment be evaluated. Design and management practices specifically identified in the regulations include waste application rate, or loading rate, and frequency of waste application.

The experimental approach used in this study was to select waste loading rates and to characterize treatment, including degradation, transformation, and immobilization of four hazardous wastes in two soil types. For each hazardous waste and each soil type, treatment was evaluated as a function of waste loading rate, soil moisture, and time. A combination of chemical analyses and bioassays (including general toxicity and mutagenicity assays) was used to characterize treatment endpoints, i.e., degradation, transformation, and immobilization.

The experimental approach described above was used to test the hypothesis that treatment would be achieved for each hazardous waste in both selected soil types. This approach was also used to evaluate the effect of selected design and management factors on treatment. Therefore, the scope of the study was to address the demonstration of treatment of hazardous waste using the soil as the treatment medium as expressed in the current federal HWLT regulations promulgated July 26, 1982.

WASTE CHARACTERIZATION

Treatment of a hazardous waste refers specifically to treatment of hazardous constituents contained in the waste. Standards identified in 40 CFR Part 264.272(c) (i) refer to Appendix VIII constituents listed in part 261. Where waste(s) are from an identified process, i.e., petroleum refining or wood preserving, EPA may accept analyses performed on a subset of constituents. Constituents identified in laboratory analyses for each waste evaluated in this study are presented in Waste Characterization. The subset of constituents evaluated for treatment in laboratory studies, based on literature and laboratory evaluations, included semivolatile (PAH compounds) and volatile (benzene, toluene, xylene, ethylbenzene, and naphthalene) constituents for all wastes, and pentachlorophenol for PCP sludge. Volatile constituents were evaluated only for immobilization potential in the laboratory studies.

SOIL CHARACTERIZATION

In order to evaluate the effect of soil type on the extent and rate of treatment of hazardous wastes, two soil types were chosen as treatment media. The two soil types were chosen to represent common land treatment soil, and also to provide a range of specific characteristics for evaluating treatment as a function of soil type. The soils selected were characterized for specific properties that are considered to be important in influencing land treatment. The soil types are characterized in detail in Soil Characterization.

WASTE LOADING RATE DETERMINATION

The loading rate (mass/area/application, or mg waste/kg soil) was the first design parameter determined. In order to evaluate the extent and rate of treatment, it is necessary to ensure the active microbial activity of the soil. The evaluation of the impact of hazardous wastes on indigenous soil microbial populations is important, especially for those wastes containing hazardous constituents specifically designed to inhibit biological activity, i.e., wood preserving wastes.

A battery of microbial assays was used for estimating the initial waste application rates for each waste and each soil type that were used in subsequent studies. Waste loading rates that were determined and used are discussed in Waste Loading Rate Evaluation.

A comparative study of the sensitivity of Microtox, respiration, dehydrogenase, initial nitrification activity, and soil plate counts to pentachlorophenol (PCP) and slop oil wastes in the Kidman sandy loam soil was performed to evaluate the response of commonly used bioassays to identical soil/waste mixtures.

WASTE TREATMENT IN SOIL

The degradation potential of hazardous constituents in waste(s) applied to soil is critical since degradation usually represents the primary removal mechanism for organic constituents in waste(s). The basis for biodegradation coefficient measurements is the determination of specific constituent soil concentrations as a function of time. The experimental approach to the determination of biodegradation was to characterize biodegradation as a first order kinetic rate process. The first order reaction rate constant was then used to calculate half-lives for each parameter. The half-lives calculated provided quantitative information for evaluating the extent and rate of treatment, and for comparing treatment effectiveness for each waste/soil combination as a function of design and management factors. Results and discussion concerning degradation of each hazardous waste are discussed in Waste Degradation Evaluation. (Volume 2)

A waste cannot be applied to land unless it is rendered less or nonhazardous as a result of treatment. Therefore, conversion of hazardous constituents to less toxic intermediates within the soil treatment medium was evaluated. Information concerning the toxicity reduction in each waste/soil combination was evaluated using an acute toxicity assay (Microtox assay), and a mutagenicity assay (Ames *Salmonella typhimurium*/mammalian microsome mutagenicity assay). Results and discussion of the transformation of each hazardous waste are discussed in Waste Transformation Evaluation. (Volume 2)

Evaluation of treatment also involved an investigation of the extent of migration of each hazardous waste. A loading rate based on biodegradation potential was selected for each soil/waste combination. The leaching potential was subsequently characterized for these loading rates in laboratory column studies. Partition coefficients among waste (oil), water and air for a subset of constituents were also determined for evaluation of immobilization input parameters required for the regulatory investigative treatment zone (RITZ) model developed by the U.S. EPA Robert S. Kerr Environmental Research Laboratory (RSKERL). Results obtained for evaluation of the immobilization of each hazardous waste are described in Waste Immobilization Evaluation. (Volume 2)

MATHEMATICAL MODEL FOR SOIL-WASTE PROCESSES

A mathematical description of the soil/waste system provides a unifying framework for the evaluation of laboratory screening and field data that is useful for the determination of soil treatment potential for a waste. While current models cannot be relied upon for long-term predictions of absolute contaminant concentrations due to the lack of an understanding of the biological, physical, and chemical complexity of the waste/soil environment, they represent powerful tools for ranking design, operation, and maintenance alternatives as well as for the design of monitoring programs.

Short (1986) developed a model (RITZ) for evaluating volatilization-corrected degradation and partitioning of organic constituents in soil systems. The model is generally based on the approach used by Jury et al. (1983) for modeling pesticide fate in soil. The RITZ model has been expanded at Utah State University to incorporate features that increase its utility for the planning and evaluation of treatment for land/waste systems.

A mathematical description of soil/waste systems provides a framework for:

(1) Evaluation of literature and/or experiment data;

(2) Evaluation of the effects of site characteristics on treatment performance (soil type, soil horizons, soil permeability);

(3) Determination of the effects of loading rate, loading frequency, soil moisture, and amendments to increase degradation on soil treatment performance;

(4) Evaluation of the effects of environmental parameters (season, precipitation) on soil treatment performance; and

(5) Comparison of the effectiveness of treatment using different practices in order to maximize soil treatment.

The extended version of the model is programmed for the computer in such a way that additional enhancements (such as unsteady flow and time variable decay transport/partition coefficients) may be incorporated into the model in the future. A summary of the model is provided in Appendix B of Volume 2 of this report.

SECTION 2

CONCLUSIONS

Specific conclusions based on project objectives and research results presented in Volume 1 include:

(1) A literature assessment for each candidate waste type and for specific hazardous constituents that were experimentally identified in each waste indicated a potential for achieving treatment in soil systems.

(2) Chemical characterization of all four wastes by GC/MS, GC, and HPLC identified the polycyclic aromatic hydrocarbon (PAH) class of semivolatile constituents as common to each waste. The acid extract fraction of the PCP wood preserving waste contained some dibenzo-p-dioxins and dibenzofurans in addition to pentachlorophenol; but no tetrachlorodibenzodioxins were detected.

(3) A comparative study of the sensitivity of five microbial assays including Microtox, soil respiration, soil dehydrogenase, soil nitrification, and viable soil microorganism plate counts for selection of initial loading rates indicated that the Microtox, soil dehydrogenase, and soil nitrification assays were the most sensitive to the presence of hazardous wastes; use of these assays would result in selecting initial loading rates at lower levels. Soil respiration (carbon dioxide evolution) and viable soil microorganism plate counts were less sensitive to hazardous waste application; use of these assays would result in the selecting higher initial loading rates.

(4) Soil loading rate studies indicated that the Microtox assay was more sensitive to changes in waste loading rate than CO_2 evolution assay. Based on results of microbial assays, loading rates selected for evaluation in long-term treatability studies were an order of magnitude higher for petroleum refinery wastes than for wood preserving wastes.

SECTION 3

RECOMMENDATIONS

Based on the results of this research investigation, the following sets of recommendations are made pertaining to loading rates and soil treatment for hazardous wastes:

(1) A combination of data sources should be used to evaluate loading rates and soil treatment potential for hazardous wastes; these data sources should include literature sources, laboratory analyses of the candidate waste for identification and quantification of hazardous constituents, characterization of the proposed soil for treatment, and laboratory studies for evaluation of treatment potential.

(2) Specific analyses for parameters that are used in the proposed U.S. EPA treatment zone model for the assessment of soil treatment potential are also recommended so that a common data base can be established for use in future assessments of the potential for treatability of specific hazardous wastes in soil.

(3) A battery of microbial assays is recommended for use in selecting initial waste loading rates; the battery should include assays that assess specific metabolic activities as well as gross microorganism viability; a final set of waste loading rates should be selected only after identifying the detoxification and immobilization potentials of soil/waste mixtures in long-term treatability studies.

SECTION 4

LITERATURE REVIEW

INTRODUCTION

Treatment in soil systems may represent a significant engineering method for control/treatment and ultimate disposal of selected hazardous constituents in applied waste. Land application for the assimilation and treatment of hazardous constituents is a potentially significant cost-effective, environmentally safe, low energy technology that has been successfully utilized for a multitude of domestic and industrial wastes. Soil systems for treatment of a a variety of industrial wastes, including food processing, organic chemical manufacturing, coke industries, textiles, and pulp and paper have been utilized for many years (Overcash and Pal 1979). However, Phung et al. (1978) reported that routine application of industrial hazardous wastes onto the soil surface and incorporation into the soil for treatment is not widely practiced, except for the oil refining industry. There are few definitive data in the literature quantifying treatment rates in full-scale soil treatment systems (Huddleston et al. 1986).

Land treatment is defined in RCRA as the hazardous waste management technology pertaining to application and/or incorporation of waste into the upper layers of the soil in order to degrade, transform or immobilize hazardous constituents contained in the applied waste (40 CFR Part 264, Subpart M). Land treatment also has been defined as the controlled application of hazardous wastes onto or into the aerobic surface soil horizon, accompanied by continued monitoring and management, in order to alter the physical, chemical, and biological state of the waste via biological degradation and chemical reactions in the soil so as to render such waste nonhazardous (Brown et al. 1983).

The current regulatory requirement for demonstrating treatment, i.e., degradation, transformation, and/or immobilization of hazardous waste constituents in soil systems, can be addressed using several approaches. Information concerning each treatment component can be obtained from several sources including literature data, field tests, laboratory studies, laboratory analyses, theoretical parameter estimation methods, or, in the case of existing units, operating data (40 CFR Part 264.272). It is suggested that a combination of data sources should be utilized, e.g., literature data, laboratory analyses, laboratory studies and field verification tests, to strengthen confirmation of hazardous constituent treatment demonstration. The availability and completeness of existing literature data will influence the need for further collection of performance data. The U.S. EPA considers the use of only literature data as insufficient to support a demonstration of treatment at the present time.

In this project, representative hazardous wastes from two industrial categories, wood preserving and petroleum refining, were used to evaluate the impact of waste loading on soil assimilative capacity in land treatment systems. A comprehensive assessment of literature available for each waste type was conducted as an aid in making these evaluations.

WOOD PRESERVING INDUSTRY

Introduction

The wood preserving industry, as defined in Standard Industrial Classification (SIC) 2491, is comprised of establishments primarily engaged in treating wood, which are sawed or planed in other establishments, with creosote or other preservatives to prevent decay and to protect against fire and insects. This industry also includes the cutting, treating, and selling of crossties, poles, posts, and piling. Wood preservation increases the life of wood products by decades, which reduces the demand for wood production. Thus wood preserving allows time for renewal of timber resources.

Process Description

Wood preservation is a two-stage process: 1) conditioning the wood to reduce its natural moisture content and to increase permeability and 2) treating the wood with the preservative (Sikora 1983). Several methods have been used for conditioning the wood, including: seasoning in open yards; steam conditioning; vapor drying; kiln drying; controlled air seasoning and tunnel drying. After the wood is conditioned, it is immersed in preservative chemicals, either at ambient or elevated temperatures, and either with or without the use of pressure.

The use of wood preservatives has been restricted by the U.S. EPA to certified applicators.

Characteristics of Wood Preservatives

Desirable properties of wood preservatives are: 1) inhibitory effects on wood-destroying organisms, 2) permanence, i.e., preservation effects should be sustained for long periods of time, and 3) freedom from objectionable qualities (i.e., health hazards, fire hazards, corrosiveness, and reduced strength of the treated wood).

Two major types of wood preservatives include creosote and pentachlorophenol (PCP). Creosote is used primarily for railroad ties, utility poles, and pilings, and PCP for utility poles, cross arm posts, and lumber (Sikora 1983).

Creosote is made by high-temperature carbonization of bituminous coal. The high temperature results in a complex mixture of organic compounds consisting mainly of aromatic hydrocarbons, tar acids (phenolic derivative of the aromatic compounds), and tar bases (heterocyclic compounds containing nitrogen plus some neutral oxygenated compounds). Principal constituents of high temperature creosote wood preservatives as reported by various investigators are shown in Tables 1 and 2. The major polynuclear aromatic hydrocarbons (PAHs) present are two, three, and four ring compounds and their methyl derivatives. Creosote may also contain small amounts of five and six ring PAH compounds, some of which are suspected or recognized carcinogens as pure compounds. Concentrations of inorganic constituents are typically low in creosote. Creosote alone or in combination with coal tar or petroleum is the major preservative used in the wood pressure treating industry (Merrill and Wade 1985).

TABLE 1. PRINCIPAL CONSTITUENTS OF HIGH-TEMPERATURE CREOSOTE (WINSLOW 1973)

Compound	% by Weight
Naphthalene	7 - 28
Phenanthrene	9 - 14
Acenaphthene	2 - 5
Fluoranthene	2 - 5
Fluorene	2 - 4
Methylnaphthalenes	1 - 4
Pyrene	2 - 3
Carbazole	1.8-2.7
Anthracene	1.2-1.8
Diphenylene oxide	0.5-1.0
9,10-Dihydroanthracene	0.1-0.3

Commercial PCP contains 85-90 percent PCP, 3-8 percent of tetrachlorophenols, 2-6 percent other chlorinated phenols, and the remainder consists of other chlorinated compounds and inert materials (Crosby 1981). Properties of PCP are shown in Table 3. When used as a wood preservative, PCP is usually mixed with petroleum products or added to creosote. PCP is of environmental concern due to its toxicity to humans and to aquatic life. The level of impurities in PCP may also be important, for most technical PCP samples contain the higher-chlorinated dibenzodioxins and dibenzoflurans. The dioxin usually present in the highest concentration is the comparatively nontoxic octachlorodibenzo-p-dioxin (OCDD). The highly toxic tetrachlorodibenzo-p-dioxin (TCDD) is not present, but the toxic hexachlorodibenzo-p-dioxin (HCDD) and heptachlorodibenzo-p-dioxin (HpCDD) isomers are usually present (Crosby 1981). Other impurities may include predioxins, isopredioxins, poly-chlorodiphenyl ethers, cyclohexadienones, and chlorinated hydrocarbons (Crosby 1981).

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TABLE 2. SPECIFIC COMPONENTS IN CREOSOTE OIL (LORENZ AND GJOVIK 1972)

Component	Formula	Molecular Weight	Boiling Point, °C	Fraction in Creosote Oil (wt. pct)*
Naphthalene	$C_{10}H_8$	128.	218	3.0
2-Methylnaphthalene	$C_{11}H_{10}$	142.	241	1.2
1-Methylnaphthalene	$C_{11}H_{10}$	142.	245	0.9
Biphenyl	$C_{12}H_{10}$	154.	255	0.8
Acenaphthene	$C_{12}H_{10}$	154.	279	9.0
Dimethylnapthalenes	$C_{12}H_{12}$	156.	267-269	2.0
Dibensofuron	$C_{12}H_8O$	168.	287	5.0
Carbazole	$C_{12}H_9N$	167.	355	2.0
Fluorene	$C_{13}H_{10}$	166.	297	10.0
Methylfluorenes	$C_{14}H_{12}$	180.	318	3.0
Phenanthrene	$C_{14}H_{10}$	170.	340	21.0
Anthracene	$C_{14}H_{10}$	178.	340	2.0
9,10-Dihydroanthracene	$C_{14}H_{12}$	180.	312	-
Methylphenanthrenes	$C_{15}H_{12}$	192.	354-355	3.0
Methylanthracenes	$C_{15}H_{12}$	192.	360	4.0
Fluoranthene	$C_{16}H_{10}$	202.	382	10.0
Pyrene	$C_{16}H_{10}$	202.	393	8.5
Benzofluorenes	$C_{17}H_{12}$	216.	413	2.0
Chrysene	$C_{18}H_{12}$	228.	448	3.0
Benz(a)anthracene	$C_{18}H_{12}$	228.	438	-
Benz(j)fluoranthene	$C_{10}H_{12}$	252.	480	-
Benz(k)fluoranthene	$C_{20}H_{12}$	252.	480	-
Benz(a)pyrene	$C_{20}H_{12}$	252.	496	-
Benz(e)pyrene	$C_{20}H_{12}$	252.	493	-
Perylene	$C_{30}H_{12}$	252.	460	-
Benzo(b)chrysene	$C_{22}H_{14}$	278.	500	-
TOTAL				90.4

*Values shown are "approx. pct. ± 0.7%." Analysis was by gas chromatography with flame ionization detection using a reference mixture of compounds "as a quantitative and qualitative standard for calibrating the gas chromatograph." The origin of the creosote sample used was not described.

TABLE 3. SELECTED PHYSICAL PROPERTIES OF PCP (CROSBY 1981)

Property	PCP
Melting point, ^{o}C	190.2^{o}
Boiling point, ^{o}C	300.6^{o}
Vapor Pressure, Torr (mm hg)	
$0^{o}C$	1.7×10^{-5}
$20^{o}C$	1.7×10^{-4}
$50^{o}C$	3.1×10^{-3}
$100^{o}C$	0.14
$200^{o}C$	25.6
$300^{o}C$	758.4
Solubility in water (g/L)	
$0^{o}C$	0.005
$20^{o}C$	0.014
$30^{o}C$	0.020
$50^{o}C$	0.035
$70^{o}C$	0.085
Solubility in organic solvents (g/L, 25^{o})	
Methanol	180
Acetone	50
Benzene	15
pK_A (25^{o})	4.70
Partition coefficient (Kp), 25^{o}	
Octanol-water	1760
Hexane-water	1.03×10^{5}

Characteristics of Wood Preserving Wastes

The principal source of wastewaters in the wood preserving industry is from the conditioning process, while some wastewaters are produced when the treated wood product is removed and allowed to drain. The steam condensate is also a source of wastewater. The characteristics of the resulting wastewater are highly variable and depend on the conditioning method, type of preservative(s) used, type of solvent used with the preservative (coal tar, oil, etc.), and the extent of dilution with nonprocess water (boiler blowdown, rainfall, steam condensate, etc.). Wastewaters from creosote and pentachlorophenol treatment often have high phenolic, chemical oxygen demand (COD), and oil concentrations and generally appear turbid as a result of emulsified oils. Their pH is in the acidic range (4.1-6.0). Compounds that are extracted from wood (mainly simple sugars) during wood conditioning contribute to the high COD values. Wastes also result from spills, leaks and sludges from wastewater treatment processes. The amount of creosote waste sludge and PCP waste sludge produced annually by the entire industry is only 239 to 930 and 600 metric tons, respectively. However, the sludge is often allowed to accumulate for months or even years before removal and disposal (Sikora 1983).

Both a creosote sludge and a combined PCP-creosote sludge were used in this experimental investigation.

Treatment of Creosote Wastes in Soil Systems

The principal classes of organic constituents present in creosote wastes are PAHs and phenolics.

PAHs are compounds which consist of two or more fused benzene rings, with each ring sharing two or more carbon atoms. The relative stability of PAHs is related to the ring arrangement, as described in Table 4. Graphical representations of the types of ring arrangements described in Table 4 may be seen in Table 5. Solubilities of PAHs decrease as molecular weight, chain length and molecular volume increase. Properties of the 16 PAH compounds designated as U.S. EPA priority pollutants are given in Table 5.

Phenolics are low-to-moderately volatile compounds which may have antiseptic properties towards environmental organisms. Phenolics are highly soluble in water but have low vapor pressures and low sorptive tendencies. General physical properties of several phenolic compounds are shown in Table 6.

Toxicological Significance of Creosote Wastes--

The use of creosote has been restricted by the U.S. EPA to protect applicators of the preservative and users of the treated wood from unnecessary exposure. Creosote contains many constituents that are reported to be mutagenic, carcinogenic, teratogenic, fetotoxic, and/or toxic. Reported health effects of these constituents are shown in Table 7. Descriptions of documented cases of human health effects of creosote are shown in Table 8.

TABLE 4. RING ARRANGEMENT AND RELATIVE STABILITY OF PAH COMPOUNDS (BLUMER 1976)

Ring Arrangement	Description	Stability*	Examples
Linear	all rings in line	least	anthracene tetracene
Cluster	at least one ring surrounded on three sides	intermediate	pyrene benzopyrene
Angular	rings in steps	most	phenanthrene chrysene

*Chemical stability in the environment from least to most stable.

Bos et al. (1983, 1984) determined that mutagenicity of creosote was probably due to the presence of mutagenic aromatic hydrocarbons, including benzo(a)pyrene and benz(a)anthracene. The authors suggested, that since these compounds are probably not essential for wood-preserving properties of creosote, a more selective composition of the product by control of distillation temperature should be considered.

Polynuclear azaarenes, which are polycyclic aromatic bases such as quinolines, isoquinolines, benzoquinolines, and alkayl- and benzo-substituted azanaphthalenes, have been detected in creosote-pentachlorophenol wastewaters (Table 9). These compounds have been reported to be toxic, teratogenic, mutagenic, and/or carcinogenic (Adams and Giam 1984).

Additional information concerning health effects of constituents found in creosote may be found in the U.S. EPA health effects assessment documents for PAHs (U.S. EPA 1984e) benzo(a)pyrene (U.S. EPA 1984b), and coal tars (U.S. EPA 1984c).

Degradation and Immobilization of PAH and Phenolic Compounds--

Microbial metabolism of PAHs has been studied primarily using pure cultures and single-compound, laboratory-scale systems. There are few reports of PAH biodegradation under field conditions and even fewer concerning soil systems specifically.

A wide range of soil organisms, including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae, have been shown to have the enzymatic capacity to oxidize PAHs. Prokaryotic organisms, bacteria, and cyanobacteria, use different biodegradation pathways than the eukaryotes, fungi, and algae, but both involve molecular oxygen.

TABLE 5. PROPERTIES OF 16 PRIORITY POLLUTANT PAH COMPOUNDS

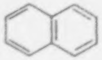
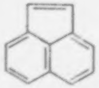
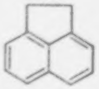
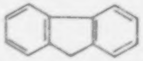
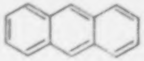
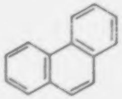
		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* °C	Boiling Point* °C	Vapor pressure @ 20°C torr	Log K_{ow}*	Length of Molecule A°	K_{oc}
1. Two Rings Naphthalene		128	31,700	80	218	4.92×10^{-2}	3.37	8.0	1,300⁺
2. Three Rings Acenaphthylene		152	3,470	92	265	2.9×10^{-2}	4.07		
Acenaphthene		154	3,930	96	279	2.0×10^{-2}	4.33		
Fluorene		166	1,980	116	293	1.3×10^{-2}	4.18		
Anthracene		178	73	216	340	1.96×10^{-4}	4.45	10.5	2,600⁺
Phenanthrene		178	1,290	101	340	6.80×10^{-4}	4.46	9.5	23,000⁺

TABLE 5. CONTINUED

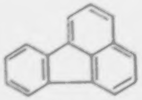
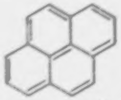
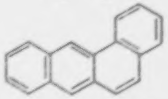
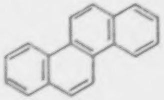
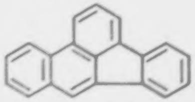
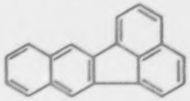
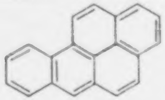
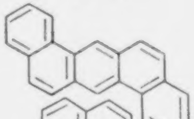
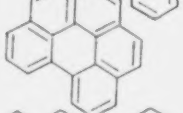
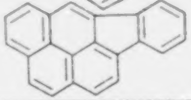
		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* °C	Boiling Point* °C	Vapor pressure @ 20°C torr	Log K_{ow}*	Length of Molecule A°	K_{oc}
3. Four Rings Fluoranthene		202	260	111	--	6.0×10^{-6}	5.33	9.4	
Pyrene		202	135	149	360	6.85×10^{-7}	5.32	9.5	62,700[#] 84,000[+]
Benz(a)anthracene		228	14	158	400	5.0×10^{-9}	5.61	11.8	
Chrysene		228	2	255	--	6.3×10^{-7}	5.61	11.8	
4. Five Rings Benzo(b)fluoranthene		252	1.2	167	--	5.0×10^{-7}	6.57		
Benzo(k)fluoranthene		252	0.55	217	480	5.0×10^{-7}	6.84		

TABLE 5. CONTINUED

		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* ^oC	Boiling Point* ^oC	Vapor pressure @ 20^oC torr	Log K_{ow}*	Length of Molecule A^o	K_{oc}
Benzo(a)pyrene		252	3.8	179	496	$5.0x10^{-7}$	6.04		4,510,651
Dibenz(a,h)anthracene		278	2.49	262	--	$1.0x10^{-10}$	5.97	13.5	2,029,000#
5. Six Rings Benzo(g,h,i)perylene		276	0.26	222	--	$1.0x10^{-10}$	7.23		
Indeno(1,2,3-Cd)pyrene		276	62	163	--	$1.0x10^{-10}$	7.66		

*Sims and Overcash (1983).
+Karickhoff et al. (1979).
#Means et al. (1980) (mean value is reported).

TABLE 6. SUMMARY OF PHYSICAL PROPERTIES FOR SELECTED PHENOLIC COMPOUNDS (VERSAR INC. 1979)

Compound	Melting Point (°C)	Boiling Point (°C)	Aqueous Solubility (mg/l)	Log K_{ow} (octanol/water partition coefficient)	Vapor Pressure (torr at 20°C)
Phenol	40.9	181.8	93,000 (at 25°C)	1.46	0.53*
2,4-Dimethylphenol	24.5	210.9	4,200 (at 20°C)	2.50	0.06*
4,6-Dinitro-o-cresol	85.8	No Data		2.85	No Data
4-Nitrophenol	114.9	279	16,000 (at 25°C)	1.91	2.24+
2,4-Dinitrophenol	114	No Data	5,600 (at 18°C)	1.53	No Data

*Vapor pressure as a supercooled liquid.
+Vapor pressure at 146°C.

TABLE 7. HEALTH EFFECTS OF CHEMICAL CONSTITUENTS OF CREOSOTE (U.S. EPA 1984a)

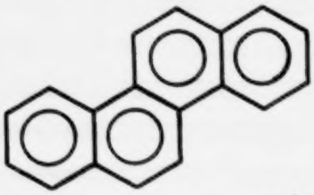
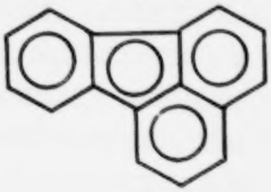
Compound	Effect
1. Unsubstituted 6-membered aromatic ring systems	
	
chrysene	mutagenic initiator, carcinogenic
pyrene	co-carcinogen (with fluoranthene benzo[a]pyrene), mutagenic
benzo[a]pyrene	mutagenic carcinogenic, fetotoxic, teratogenic
benzo[e]pyrene	carcinogenic, mutagenic
benzo[a]anthracene	mutagenic, carcinogenic
benzo[a]phenanthrene	initiator, mutagenic
naphthalene	inhibitor
phenanthrene	initiator, mutagenic
anthracene	mutagenic
dibenzanthracene	mutagenic
acenaphthene	mutagenic
triphenylene	mutagenic
2. Unsubstituted aromatic ring systems containing 5-numbered rings	
	
fluoranthene	co-carcinogenic, initiator, mutagenic
benz[j]fluoranthene	carcinogenic, mutagenic
fluorene	mutagenic

TABLE 7. CONTINUED

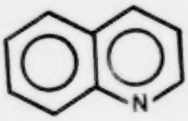
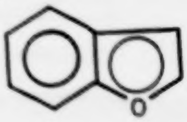
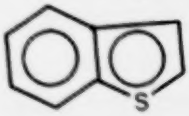
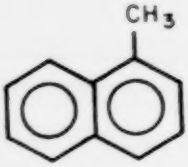
Compound	Effect
3. Heterocyclic nitrogen bases	
quinoline	carcinogenic
indole	mutagenic
benzocarbazoles	carcinogenic
isoquinoline	mutagenic
1-methyl isoquinoline	possibly carcinogenic
3-methyl isoquinoline	possibly carcinogenic
5-methyl quinoline	possibly carcinogenic
4-methyl quinoline	possibly carcinogenic, mutagenic
6-methyl quinoline	possibly carcinogenic
5-methyl isoquinoline	possibly carcinogenic
7-methyl isoquinoline	possibly carcinogenic
6-methyl isoquinoline	possibly carcinogenic
1,3-dimethyl isoquinoline	possibly carcinogenic
acridine	mutagenic
carbazole	mutagenic
4. Heterocyclic oxygen and sulfur compounds	
coumarone 	No effects found in the literature for this structural class.
thionaphthene 	
5. Alkyl substituted compounds	
1-methyl naphthacene	mutagenic
2-methyl anthracene	mutagenic
methyl fluoranthene	possibly carcinogenic
1-methyl naphthalene	inhibitor
2-methyl naphthalene	inhibitor
ethyl naphthalene	inhibitor
2,6-dimethyl naphthalene	inhibitor
1,5-dimethyl naphthalene	inhibitor
2,3-dimethyl naphthalene	accelerator
2,3,5-trimethyl naphthalene	inhibitor
2,3,6-trimethyl naphthalene	accelerator
methyl chrysene	initiator
1,4-dimethyl phenanthrene	initiator, mutagenic
1-methylphenanthrene	mutagenic

TABLE 7. CONTINUED

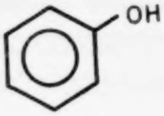
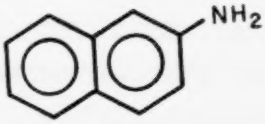
Compound	Effect
6. Hydroxy compounds	
	
phenol	promoter
p-cresol	promoter
o-cresol	promoter
m-cresol	promoter
7. Aromatic amines	
	
2-naphthylamine	carcinogenic
p-toluidine	carcinogenic
o-toluidine	carcinogenic
2,4-xylidine	carcinogenic
2,5-xylidine	carcinogenic
8. Paraffins and naphthenes	
$\left[-CH_2-\right]_n$	(n is large, e.g., greater than 15)
No effects found in the literature for this structural class.	

TABLE 8. HUMAN HEALTH EFFECTS OF EXPOSURE TO CREOSOTE (U.S. EPA 1974)

Year	Substance Tested	Occupation of Exposed Individual	Type of Tumor Response
1896	Handling of Creosote	Worker who dipped railway ties in creosote	Warty elevation on arms; Papillomatous swellings on scrotum
1920	Handling of Creosote	Workers who creosoted timbers	Skin cancer
1924	Handling of Creosote	Creosote factory worker	Squamous epitheliomata on hand; epitheliomatous deposits in liver, lungs, kidneys and heart walls
1947	Handling of Creosote	37 men of various occupations	Cutaneous epitheliomata
1956	Painting of Creosote	Shipyard worker	Malignant cutaneous tumors of the face

TABLE 9. POLYNUCLEAR AZAARENES IN CREOSOTE-PCP WOOD PRESERVATIVE WASTEWATER (ADAMS AND GLAM 1984)

Compound*	Concentration ($mg\ kg^{-1}$)
Quinoline	260
Isoquinoline	69
2-methylquinoline	55
8-methylquinoline	11
C_1-azanaphthalene	95
7-methylquinoline	38
C_1-azanaphthalenes	47
2,6-/2,7-dimethylquinoline	21
C_2-azanaphthalenes	66
Methylvinylazanaphthalenes	14
C_3-azanaphthalene	12
4-azafluorene	16
7,8-benzoquinoline	53
acridine	55
5,6-benzoquinoline/phenanthridine	71
C_1-benzoazanaphthalenes	350
Vinylbenzoazanaphthalene	3.0
Azafluoranthenes/azapyrenes	54
C_1-azafluoranthenes/azapyrenes	4.4
Dibenzoazanaphthalenes	5.2
Total	1300

*C_1, C_2, and C_3 = methyl-, dimethyl- or ethyl-, and trimethyl- or propyl substituents, respectively.

Two and three-ring PAH compounds can be utilized by soil microorganisms as a sole carbon source and are usually easily degraded. In a study by McKenna and Heath (1976), naphthalene and phenanthrene were rapidly oxidized by both Pseudomonas and Flavobacterium, while anthracene was metabolized at a moderate rate by Flavobacterium. No appreciable degradation of four- and five- ring compounds was detected.

Compounds such as naphthalene, phenanthrene, and anthracene, which are readily metabolized, are relatively water soluble, while persistent PAHs, such as chrysene and benzo(a)pyrene, have a lower water solubility. Exceptions exist with pyrene and fluoranthene in that these compounds are more soluble than anthracene and yet have not been found by some researchers (Graenewegen and Stolp 1981) to be appreciably metabolized by soil microorganisms. Other factors that may result in the persistence of PAH compounds are insufficient bacterial membrane permeability to the compounds, lack of enzyme specificity and lack of aerobic conditions (Overcash and Pal 1979).

Two incubation studies were performed by Bulman et al. (1985) to assess PAH loss from soil. In the first, a mixture of eight PAH's [naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(a)pyrene] was added to soil at levels of 5 and 50 $mg \cdot kg^{-1}$ and the concentration of each compound was monitored with time. In the second, ^{14}C labelled benzo(a)pyrene and anthracene were added to soil in biometer flasks. The distribution of ^{14}C as volatile, adsorbed and degraded products was determined in sterilized and biologically active soil. These studies were performed using unacclimated agricultural soil. Naphthalene, phenanthrene, anthracene, pyrene and fluoranthene initially disappeared rapidly from soil during an initial period of 200 days or less. A loss of 94 to 98 percent occurred during this initial period and approximated first order kinetics, in some cases following a lag period. Within the initial period, with the exception of anthracene, the first order kinetic rate constants were the same for 5 and 50 $mg \cdot kg^{-1}$ additions of PAH. Following the initial period, the remaining 2-6 percent of the added PAH was lost at a much reduced rate and the first order rate constants tended to be higher with the 50 $mg \cdot kg^{-1}$ addition than the 5 $mg \cdot kg^{-1}$ addition of PAH. Losses of only 22 to 88 percent were observed for benzo(a)anthracene, chrysene and benzo(a)pyrene and only one kinetic period was identified within the 400-day incubation period. With chrysene the first order kinetic rate constants were the same at the 5 and 50 $mg \cdot kg^{-1}$ levels of addition, however, for benzo(a)anthracene and benzo(a)pyrene the rate constants differed. The disappearance of benzo(a)anthracene approximated first order kinetics; however a zero order model was generally appropriate for the disappearance of benzo(a)pyrene and chrysene.

The mechanisms of disappearance of anthracene and benzo(a)pyrene were assessed using ^{14}C labelling. The results indicated that biological activity was responsible for some of the loss of anthracene from soil. Binding to soil solids and volatilization (either as anthracene or as metabolites) were identified as the major loss mechanisms. Identification of loss mechanisms for benzo(a)pyrene was less successful due to the small amount of benzo(a)pyrene that reacted within the incubation period. Binding of benzo(a)pyrene to soil solids appeared to be the major mechanism involved, while microbial transformation of the compound was minimal.

Torstensson and Stenstrom (1986) have cautioned, however, that an indirect measurement of disappearance, such as liberated $^{14}CO_2$ from a ^{14}C-labeled compound is not always reliable. They recommend that the rate of decomposition of a substance should be defined by direct measurement of its disappearance. Liberation of CO_2 may not be concurrent with degradation because of accumulation of metabolites in the soil.

PAHs with a greater number of rings are not known to be utilized as a sole carbon source but have been reported to be cometabolized with other organic compounds. This process involves the concurrent metabolism of a compound that a microorganism is unable to use as a sole source of energy with a carbon source capable of sustaining growth. In a study by McKenna and Heath (1976), the cometabolism of refractory PAH compounds in the presence of two- and three-ring PAH compounds was investigated. The degradation of pyrene, 3,4-benzpyrene, 1,2-benzanthracene, and 1,2,5,6-dibenzanthracene in the presence and in the absence of phenanthrene was measured. Separate cultures of Flavobacterium and Pseudomonas were maintained in the presence of each of the PAH compounds. Both Flavobacterium and Pseudomonas exhibited negligible utilization of the refractory PAH compounds in the absence of phenanthrene. However, Flavobacterium, in the presence of phenanthrene, was able to significantly degrade all four test compounds. Cometabolism by Pseudomonas was not observed. In a similar experiment PAH compound degradation by a mixed culture was measured. For each PAH compound studied, one container of inoculum received naphthalene as a growth substrate while a second container received phenanthrene as a growth substrate. Cometabolism of pyrene, 1,2-benzanthracene, 3,4-benzpyrene, and 1,2,5,6-dibenzanthracene by the mixed culture was exhibited in the presence of either naphthalene or phenanthrene.

The fate of PAH compounds in terrestrial systems have been reviewed by Sins and Overcash (1983), Edwards (1983), and Cerniglia (1984). These reviews present additional information on PAH degradation.

Phenolics in general are readily degraded, with most having biodegradation half-lives of only days. The effect of phenols on soil microorganisms is dependent on the soil concentration or amount added (Overcash and Pal 1979). At low doses (0.01-0.1 percent of soil weight), the phenol serves as an available substrate, and there is an increase in microbial numbers. As the dose level is increased (0.1-1.0 percent of soil weight), an increasingly strong inhibitory or sterilizing effect is noted. At these levels, a partial sterilization occurs in which there is a depression in microbial numbers, but not a complete die-off. After a period of time, microbes adapt or phenol is lost through sorptive inactivation or volatilization and a regrowth of population occurs.

Microbial degradation of phenol has been observed in many laboratory studies in which phenol represented the primary carbon source for isolated and adapted microorganisms. Happold and Key (1932) were among the first to demonstrate the bacterial degradation of phenol in phenolic wastes. Alexander and Lustigman (1966) observed that phenol was degraded rapidly by a mixed population of soil microorganisms. Their data suggested that the hydroxy group, compared to other benzene ring substituents, facilitated microbial degradation.

Bayly et al. (1966) reported that Pseudomonas putida converted phenol to catechol. Verschueren (1977) reported complete disappearance of phenol in a soil suspension in two days. The effect of temperature variations on the rate of biodegradation of phenol in the soil was studied by Medvedev and Davidov (1972). At 5°C, phenol remained in the soil after 16 days, while at 19°C there was complete loss after six days. The ability to degrade phenol improved with successive phenol doses (Medvedev et al. 1975). Initial degradation of phenols in soils has been enhanced by bacterial seeding of Pseudobacterium lacticum and Pseudomonas liquefaciens (Dolgova 1975).

Other phenolic compounds such as 2,4-dimethylphenol, 4-nitrophenol, 4,6-dinitro-o-cresol, and 2,4-dinitrophenol have also been shown to be readily degraded in soil (Medvedev and Davidov 1972, Verschueren 1977, Overcash et al. 1982).

A summary of degradation of PAHs and phenolic compounds is given in Table 10. The term half-life of the compounds is used to indicate the persistence of a chemical in the soil, water, or air environment. The half-life is the time required for the concentration of a compound to decrease to one-half of its initial value. Half-lives may be estimated from first-order kinetics, if first order rate constants are known for waste constituents. Performance data indicate that the degradation of most chemicals in the soil can be modeled using a first-order reaction rate (i.e., $dC/dt = -KC$, where at any one time, t, the rate of degradation is proportional to the concentration, C, of the chemical in the soil (ERT 1985b)). First-order kinetics generally apply where the concentration of the chemical being degraded is low relative to the biological activity in the soil (Kaufman et al. 1983). At very high chemical concentrations, Michaelis-Menten kinetics appear to apply, and the rate of degradation changes from being proportional to the concentration to being independent of concentration (Hamaker 1966; Hamaker et al. 1967). For compounds such as PCP, which serves both as a growth substrate and, at higher concentrations, as a growth inhibitor, the Haldane modification of the Monod equation has been shown to be suitable to describe the kinetics of degradation (Klecka and Maier 1985).

From information given in Table 10, initial rates of degradation of PAH compounds in soil as a function of initial soil concentrations, assuming first order kinetics, are presented in Figure 1. These data are corrected for variations in temperature using an Arrhenius equation with coefficients developed from PAH data to a temperature of 20°C, $\theta = 1.013$. Rates were normalized to µg PAH transformed/g soil-dry wt/hr. The general trends shown in Figure 1 can be summarized as follows: 1) for a given PAH compound the initial rate of transformation increases with increasing initial soil concentration, 2) within the class of polycyclic aromatic compounds, the initial rate of transformation decreases with increasing number of fused benzene rings (or molecular size).

TABLE 10. KINETIC PARAMETERS DESCRIBING RATES OF DEGRADATION OF PAH AND PHENOLIC COMPOUNDS IN SOIL SYSTEMS (SIMS AND OVERCASH 1983, ERT 1985b)

Substance	Initial Concentration (μg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Phenol	500	0.693	1.0	Medvedev & Davidov (1972)
Phenol	500	0.315*	2.2*	Medvedev & Davidov (1972)
2,4-dimethylphenol	500	0.35-0.69	1-2	Medvedev & Davidov (1972)
4,6-dinitro-o-cresol	--	0.023	30	Versar, Inc. (1977)
2,4-dinitrophenol	5-50	0.025	28	Overcash et al. (1982)
2,4-dinitrophenol	20-25	0.099-0.23	3-7	Sudharkar-Barik & Sethunathan (1978)
4-nitrophenol	--	0.043	16	Verschuerer (1977)
Pentachlorophenol	--	0.018	28	Murthy et al. (1979)
Naphthalene	7	5.78	0.12	Herbes & Schwall (1978)
Naphthalene	7	0.005*	125*	Herbes & Schwall (1978)
Naphthalene	7	0.173	4^{+}	Herbes & Schwall (1978)
Acenaphthylene	0.57	0.039	18	Sims (1982)
Acenaphthylene	57	0.035	20	Sims (1982)
Anthracene	0.041	0.019	36	Sims (1982)
Anthracene	41	0.017	42	Sims (1982)
Phenanthrene	2.1	0.027	26	Groenewegen and Stolp (1976)
Phenanthrene	25,000	0.277	2.5^{+}	Sisler and Zobell (1947)
Benz(a)anthracene	0.12	0.046*	15.2*	Herbes & Schwall (1978)
Benz(a)anthracene	3.5	0.007	102	Groenewegen & Stolp (1976)
Benz(a)anthracene	20.8	0.003	231	Gardner et al. (1979)
Benz(a)anthracene	25.8	0.005	133	Gardner et al. (1979)
Benz(a)anthracene	17.2	0.008	199	Gardner et al. (1979)
Benz(a)anthracene	22.1	0.006	118	Gardner et al. (1979)
Benz(a)anthracene	42.6	0.003	252	Gardner et al. (1979)

TABLE 10. CONTINUED

Substance	Initial Concentration (μg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Benz(a)anthracene	72.8	0.004	196	Gardner et al. (1979)
Benz(a)anthracene	0.07	0.005	134	Sims (1982)
Benz(a)anthracene	0.10	0.005	142	Sims (1982)
Benz(a)anthracene	0.15	0.005	154	Sims (1982)
Benz(a)anthracene	7	0.016	43	Sims (1982)
Fluoranthene	3.9	0.016	44	Groenewegen and Stolp (1976)
Fluoranthene	18.8	0.004	182	Gardner et al. (1979)
Fluoranthene	23.0	0.007	105	Gardner et al. (1979)
Fluoranthene	16.5	0.005	143	Gardner et al. (1979)
Fluoranthene	20.9	0.006	109	Gardner et al. (1979)
Fluoranthene	44.5	0.004	175	Gardner et al. (1979)
Fluoranthene	72.8	0.005	133	Gardner et al. (1979)
Pyrene	3.1	0.020	35	Groenewegen and Stolp (1976)
Pyrene	500	0.067	10.5	Medvedev and Davidov (1972)
Pyrene	5	0.231	3	Medvedev and Davidov (1972)
Chrysene	4.4	0	-	Groenewegen and Stolp (1976)
Chrysene	500	0.067	10.5	Medvedev and Davidov (1972)
Chrysene	5	0.126	5.5	Medvedev and Davidov (1972)
Benz(a)pyrene	0.048	0.014	50*	Herbes and Schwall (1978)
Benz(a)pyrene	0.01	0.001	694*	Herbes and Schwall (1978)
Benz(a)pyrene	3.4	0.012	57	Groenewegen and Stolp (1976)
Benz(a)pyrene	9.5	0.002	294	Gardner et al. (1979)
Benz(a)pyrene	12.3	0.005	147	Gardner et al. (1979)
Benz(a)pyrene	7.6	0.003	264	Gardner et al. (1979)
Benz(a)pyrene	17.0	0.002	420	Gardner et al. (1979)
Benz(a)pyrene	32.6	0.004	175	Gardner et al. (1979)

TABLE 10. CONTINUED

Substance	Initial Concentration (μg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Benz(a)pyrene	1.0	0.347	2^+	Shabad et al. (1971)
Benz(a)pyrene	0.515	0.347	2^+	Shabad et al. (1971)
Benz(a)pyrene	0.00135	0.139	5^+	Shabad et al. (1971)
Benz(a)pyrene	0.0094	0.002	406^*	Shabad et al. (1971)
Benz(a)pyrene	0.545	0.011	66^*	Shabad et al. (1971)
Benz(a)pyrene	28.5	0.019	37^*	Shabad et al. (1971)
Benz(a)pyrene	29.2	0	--	Shabad et al. (1971)
Benz(a)pyrene	9,100	0.018	39^+	Lijinsky and Quastel (1956)
Benz(a)pyrene	19.5	0.099	7^+	Poglazova et al. (1967b)
Benz(a)pyrene	19.5	0.139	5^+	Poglazova et al. (1967b)
Benz(a)pyrene	19.5	0.231	3^+	Poglazova et al. (1967b)
Benz(a)pyrene	130.6	0.173	4^+	Poglazova et al. (1968)
Benz(a)pyrene	130.6	0.116	6^+	Poglazova et al. (1968)
Dibenz(a,h)anthracene	9,700	0.033	21^+	Lijinsky and Quastel (1956)
Dibenz(a,h)anthracene	25,000	0.039	18^+	Sisler and Zobell (1947)

*Low temperature (<15°C)
$^+$High temperature (>25°C)

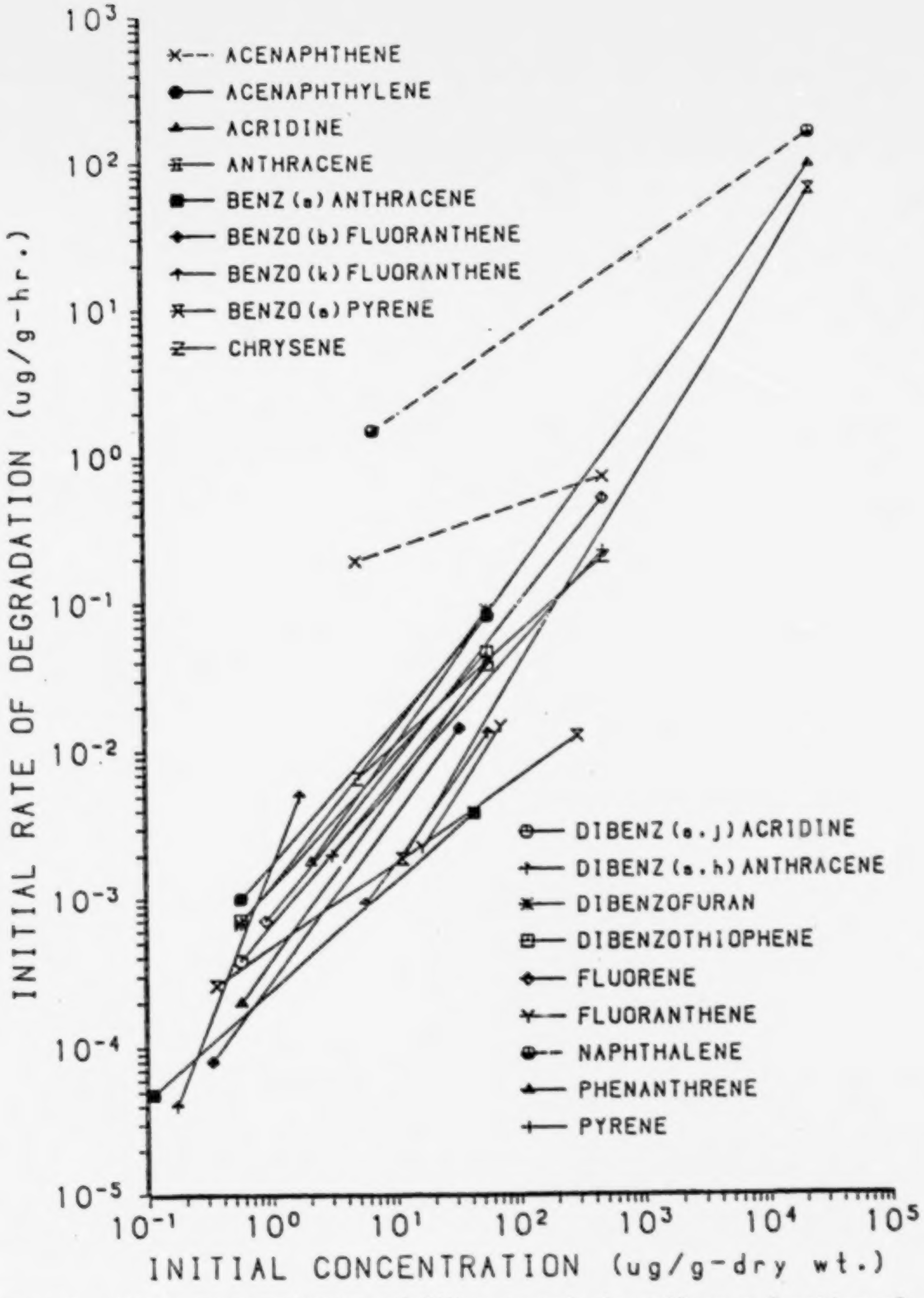


Figure 1. Rates of degradation of PAH compounds in soil as a function of initial soil concentrations (Sims and Overcash 1983).

Immobilization of PAH and Phenolic Compounds--

Quantitative descriptions of immobilization, or sorption, phenomena also contribute to the assessment of the fate of waste constituents in soil systems. Equilibrium adsorption may be described quantitatively using adsorption isotherms, which represent the relationship between the amount of a solute adsorbed and the equilibrium concentration of the solute in the soil solution at a given temperature. Specific adsorption isotherms commonly used to describe immobilization of organic constituents in soils include: 1) the Langmuir isotherm, and 2) the Freundlich isotherm.

The Langmuir isotherm adsorption relationships occur when there is no strong competition from the solvent for sorption sites on the adsorbent surface. The Langmuir adsorption isotherm is expressed mathematically using the following relationship:

$$S = \frac{K_1 K_2 C}{1 + K_2 C}$$

where S is the mass of adsorbed solute per unit mass adsorbent, K_1 represents the maximum mass of solute that can be adsorbed by the soil matrix, K_2 is a measure of the bond strength holding the sorbed solute on a soil surface, and C is the equilibrium concentration in the soil solution. The Langmuir isotherm has been used extensively for the description of inorganic and organic constituent soil adsorption.

The Freundlich isotherm is an empirical formulation describing adsorption phenomenon and can be expressed as:

$$S = KC^N$$

where K and N = constants.

The Freundlich isotherm provides flexibility in that the use of the two equation parameters, K and N, allows the fitting of the equation to a wide range of data. It also does not require a maximum limit for the amount of substance adsorbed.

The linear form of the Freundlich isotherm may be expressed as:

$$S = k_d C$$

where k_d = distribution coefficient.

The K or k_d value is dependent on the type of soil that is acting as the adsorbing medium for a given chemical. However, a parameter normalized for the actual soil organic carbon content (OC), K_{oc}, can be used to describe soil adsorption behavior, and is defined as:

$$K_{oc} = (k_d/\%OC)*100 \text{ (linear isotherm)}$$

K_{OC} = K/%OC)*100 (nonlinear Freundlich isotherm)

This parameter is less variable than non-normalized coefficients, and is normally independent of soil type.

PAHs are nonionic, nonpolar compounds that do not ionize significantly in aqueous systems. Adsorption of nonionic compounds is primarily a function of solubility. PAHs, therefore, participate in hydrophobic sorption in a soil system, where the nonpolar PAH compounds partition out of the polar water phase onto hydrophobic surfaces in the soil matrix. Hydrophobic sites include waxes, fats, and resins of the soil organic matter. The organic matter content of the soil thus is more important in determining the extent of sorption of PAHs in a soil system (Nkedi-Kizza et al. 1983) than substrate pH, soil cation exchange capacity, soil texture, or clay mineralogy (Means et al. 1980).

Table 11 summarizes the range of measured or estimated immobilization constants for the constituents known or suspected to be present in creosote wastes. The estimated range of organic partition coefficients (K_{OC}) for a given compound is based on the octanol/water partition coefficient (K_{OW}) for the compound, according to the following relationship: log K_{OC} = log K_{OW}-0.317 (Hassett et al. 1980). The K_{OC} for certain PAH compounds was estimated from reported values for PAH compounds of similar molecular weight and ring structure if no K_{OW} data were reported. Constituents with K_{OC} values greater than 10,000 are very strongly adsorbed and essentially immobilized in the soil environment. The relative mobility of PAH compounds was estimated by Umfleet (1986) to be as follows: chrysene < fluoranthene < pyrene < phenanthrene = anthracene < naphthalene.

Phenols and phenolics vary in their ability to be adsorbed by soils. The moderate values of the octanol/water partition coefficients (Table 11) for phenol, 4-nitrophenol, and 2,4-dinitrophenol indicate only a slight tendency for these compounds to be adsorbed to organic matter. 2,4-dimethyl-phenol and 4,6-dinitro-o-cresol have higher octanol/water partition coefficients and therefore show a greater potential for adsorption.

Photodecomposition of PAH and Phenolic Compounds--

Photo-oxidation of PAH compounds has been well documented (Radding et al. 1976; Versar 1979). The PAHs absorb solar radiation strongly and undergo direct photolysis. PAH compounds can be transformed into reactive cytotoxic and mutagenic intermediates following exposure to natural sunlight and other sources of radiation. Polycyclic aromatic amines (e.g., 2-aminofluorene) have especially been shown to have photomutagenic properties (Okinaka et al. 1983).

However, although direct photolysis occurs in both the atmosphere and in aqueous environments, photo-oxidation of PAHs in the soil environment is not expected to be significant because of limited exposure to light.

γ-radiation has been shown to destroy the phenol structure in aqueous solutions (Overcash and Pal 1979). Solar radiation may cause photosensitive reactions of phenolics (e.g., photonucleophilic mechanism (Overcash and Pal 1979)). Using the procedure given in U.S. EPA (1984f), the half-life of phenol in air was calculated as 1180 days.

TABLE 11. SUMMARY OF SOIL SORPTION DATA FOR CONSTITUENTS OF CREOSOTE WASTE (ERT, INC. 1985b)

Compound	No. of Rings	Molecular Weight	Solubility (mg/l)	Organic Carbon Partition Coefficient K_{oc} (ml/g)	Log Octanol/Water Partition Coefficient Log K_{ow}
Low Molecular Weight PAH					
Naphthalene	2	128	31.7	1,300	3.37
Acenaphthylene	2.5	152		1,000-10,000*	4.07
Acenaphthene	2.5		3.93	1,000-10,000*	4.33
Fluorene	3	166		1,000-10,000*	4.18
Phenanthrene	3	178	1.29	23,000	4.46
Anthracene	3	178	0.073	26,000	4.45
Fluoranthene	4	202	0.26	10,000-100,000*	5.33
Pyrene	4	202	0.135	63,000-84,000	5.32
High Molecular Weight PAH					
Benzo(a)anthracene	4	228	0.014	1,871,400	5.61
Chrysene	4	228	0.0018	100,000-1,000,000*	5.61
Benzo(b)fluoranthene	5	252	0.0012	>1,000,000*	6.57
Benzo(k)fluoranthene	5	252	0.0008	>1,000,000*	6.84
Benzo(a)pyrene	5	252	0.005	4,510,650	6.04
Dibenzo(a,h)anthracene	5	276	0.0005	2,029,000	5.97
Benzo(g,h,i)perylene	6	278			7.23
Indeno(1,2,3-cd)pyrene	6	276	0.0002	>1,000,000*	7.66
Phenolics					
Phenol		94	93,000 (25°C)	10-100*	1.46
4,6,Dinitro-o-cresol				100-1000*	2.85
4-Nitrophenol		139	16,000 (25°C)	100-1000*	1.91
2,4-Dinitrophenol		184	5,600 (18°C)	10-100*	1.53
2,4-dimethyphenol				10-1000*	

*Estimated from reported values for PAH compounds of similar molecular weight and ring structure.

Volatilization of PAH and Phenolic Compounds--

Volatilization of constituents in creosote wastes from a soil system is dependent upon several factors that include: 1) constituent vapor pressure; 2) concentration of the constituent in the soil solution; 3) soil/constituent sorption reactions; 4) solubility of the constituent in soil water; 5) solubility of the constituent in soil organic matter; 6) soil characteristics, such as temperature, water content, organic content, clay mineralogy and content, porosity, and bulk density; and 7) waste application method and tilling frequency (Spencer and Cliath 1977).

In general, since PAH compounds tend to be nonvolatile and are also readily sorbed by the soil, they do not represent a significant source of emissions from soil systems (U.S. EPA 1974). Acenaphthalene and naphthalene are the most volatile PAH compounds.

Phenolics are more volatile than other constituents of creosote, but because of their low concentrations in creosote waste, phenol emissions are not expected to be significant from creosote waste land treatment facilities.

Bioaccumulation of PAH and Phenolic Compounds--

PAHs are ubiquitous constituents of crops, plants, and algae in the natural environment. In general, leaves exhibit the highest PAH concentrations (22 to 88 ppb), and underground vegetables such as potatoes, carrots, onions, and radishes, exhibit the lowest PAH concentrations (0.01 to 6.0 ppb) (Sims and Overcash 1983).

Sources of PAHs in vegetation include anthropogenic activities resulting in PAH deposition on plants, biochemical synthesis by plants, and plant-uptake from soil (Sims and Overcash 1983). Many higher plants, however, may not take up PAHs (Blum and Swarbrick 1977).

PAHs have been demonstrated to act like plant hormones, stimulating growth and yield of higher and lower plants. Graf (1965) demonstrated the growth-promoting effects of PAHs with higher plants. He also demonstrated that the growth promoting effect was proportional to the carcinogenic potential.

There is strong evidence for plant biosynthesis of PAHs (Borneff et al. 1968). Biosynthesis of PAHs has also been investigated with respect to bacterial synthesis (Brisou 1969).

Edwards (1983), in a comprehensive review of PAHs in the terrestrial environment, presented the following conclusions concerning the uptake of PAHs in terrestrial vegetation:

1) Some terrestrial plants can take up PAHs through their roots and/or leaves and translocate them to various plant parts,

2) Uptake rates are dependent on PAH concentrations, solubility, phase (vapor or particulate), molecular size, support media anchoring the plants, and plant species,

3) PAHs may concentrate in certain plant parts more than in other parts, and

4) Some PAHs can be catabolized by plants.

Little information is available on the fate of phenolics in terrestiral systems (Overcash and Pal 1979).

Treatment of Pentachlorophenol Wastes in Soil Systems

Pentachlorophenol (PCP), a versatile biocide, is primarily used as a wood preservative and may be added to creosote to enhance the wood preservation potential of creosote. Pentachlorophenol may be used in the phenol form (PCP), as salts (e.g., sodium pentachlorophenate (Na-PCP)), or as esters (e.g., acetate or lauryl). The hydroxyl group of PCP forms esters with organic and inorganic acids. Oxidation of PCP results in the formation of pentachlorophenoxyl radicals that combine reversibly to form dimers. At low pH, PCP exists as a free acid and readily adsorbs to soil particles. At high pH , PCP exists in the ionized form (pKa = 4.7), and is more mobile. At pH 2.7, PCP is only 1 percent ionized, while at pH 6.7, it is 99 percent ionized. Alkaline salts of PCP, such as sodium pentachlorophenate (Na-PCP) are more mobile than PCP and less likely to be immobilized in a soil system.

The vapor pressure of 760 mm of pentachlorophenol is achieved at 300.6^{o}C, but even at ambient temperatures, PCP is relatively volatile. Na-PCP, however, is nonvolatile. PCP is slightly soluble in water and is soluble in most organic solvents (Table 4), while Na-PCP is more soluble in water.

Except for hydroxyl reactions, PCP is quite stable. However, it absorbs and is rapidly degraded by UV light and would not be expected to persist in the open environment (although it remains unchanged for long periods in treated wood).

The environmental chemistry of PCP was reviewed by Crosby (1981). Information concerning the uses of PCP, chemical and physical properties, biological uptake and transformation of PCP and its impurities, analytical methods for PCP and its impurities, and environmental residues of PCP and associated compounds are summarized in this review.

Toxicological Significance of PCP Wastes--

The toxicity of PCP and potential for uptake by organisms are pH-dependent, since PCP is a weak acid with a pKa of about 10^{-5}. Both bioaccumulation and toxicity increase as pH decreases, due to the greater penetration of cell membranes by un-ionized PCP molecules than by pentachlorophenate ions.

In general, PCP is a biocide toxic to microorganisms (as it is a bactericide and fungicide), to lower and higher plants (algicide, herbicide), to invertebrate and vertebrate animals (insecticide, molluscicide), and is also toxic to man. Adverse effects to man include serum enzyme induction (Klemmer 1972), low-grade infections and inflammation (Klemmer et al. 1980), and depressed kidney function (Begley et al. 1977). Technical grade PCP, with associated impurities, dibenzodioxins and dibenzofurans, produces chloracne and liver damage (Crosby 1981). Additional information concerning human health effects are presented in the U.S. EPA health effects assessment document for PC (U.S. EPA 1984d).

The U.S. EPA (1986a) has summarized the effects of PCP on aquatic life in order to develop ambient water quality criteria for PCP. The authors of the report found that the acute and chronic toxicity of PCP to freshwater animals increases as pH and dissolved oxygen concentration of the water decreases. Generally, toxicity also increases with increased temperature. The estimated acute sensitivities of 32 species at pH = 6.5 ranges from 4.355 µg/L for larval common carp to >43,920 µg/L for a cray fish. At pH = 6.5, the lowest and highest estimated chronic values of <1.835 and 79.66 µg/L, respectively, were obtained with different cladoceran species. Chronic toxicity to fish is affected by the presence of impurities, with certain industrial grades of PCP being more toxic than a purified (99+ percent) form. Freshwater algae were affected by concentrations as low as 7.5 µg/L, whereas vascular plants were affected at 296 µg/L and above. Bioconcentration factors ranged from 7.3 to 1,066 for three species of fish.

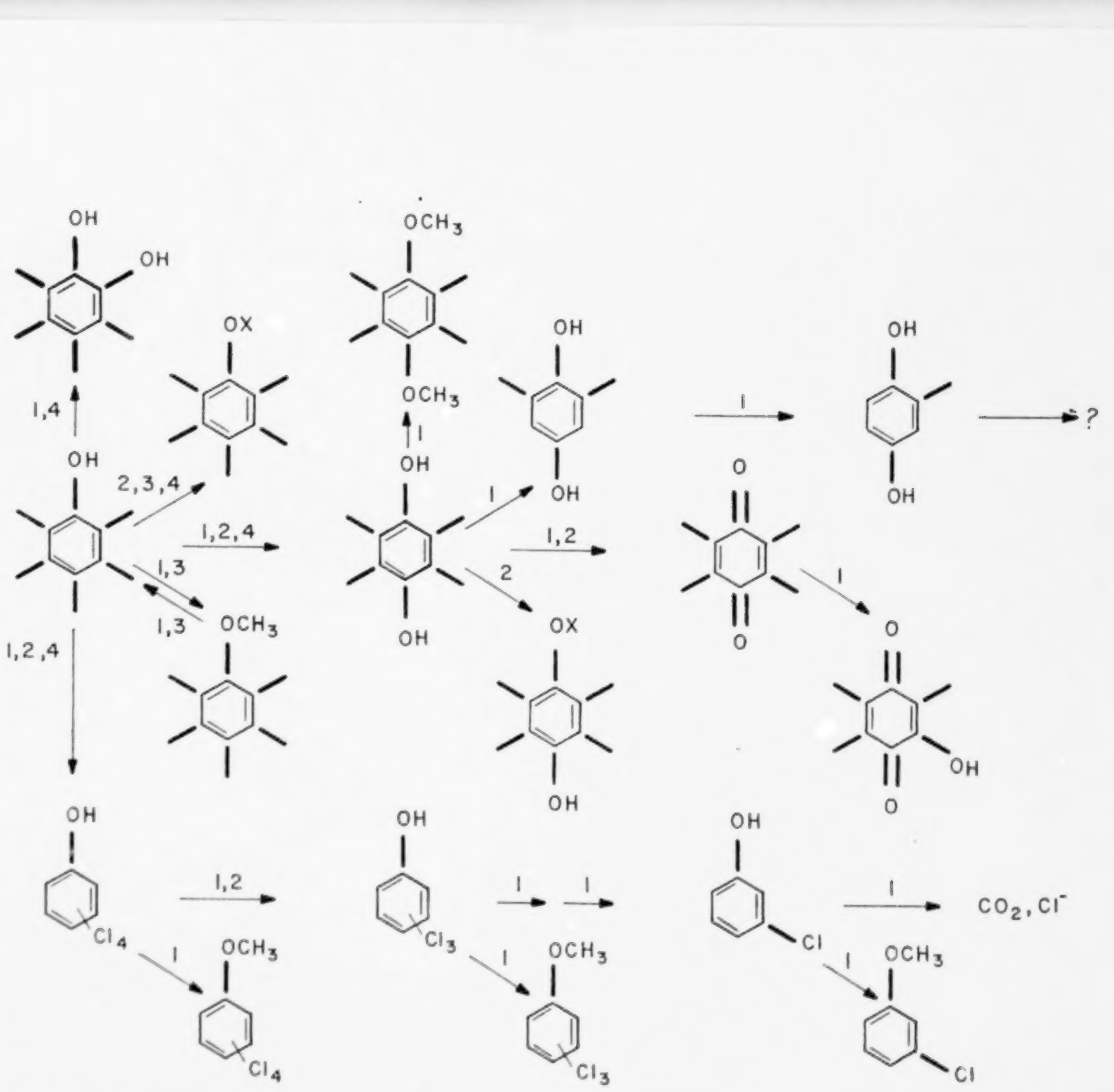
Acute toxicity values from tests with 18 species of saltwater animals, representing 17 genera, range from 22.63 µg/L for late yolk-sac larvae of the Pacific herring, Clupea harengus pallasi, to 18,000 µg/L for adult blue mussels, Mytilus edulis. Five of these values are for saltwater fish. The embryo and larval stages of invertebrates and the late larval premetamorphosis stage of fish appear to be the most sensitive life stages to PCP. With few exceptions, fish are more sensitive than invertebrates to PCP. Salinity, temperature, and pH have a slight effect on the toxicity of PCP to some saltwater animals.

The EC50s for saltwater plants range from 17.40 µg/L for the diatom, Skeletonema costatum, to 3,600 µg/L for the green algae, Dunaliella tertiolecta.

The chlorinated dioxin and dibenzofuran impurities in PCP are also of concern. The U.S. EPA has listed PCP manufacturing wastes as acute hazardous wastes because of the presence of hexachlorodioxins (U.S. EPA 1985).

Degradation and Transformation of PCP--

Despite its high degree of chlorination, PCP has been shown to be readily degraded in soil. Microbial decomposition appears to be the primary detoxification mechanism. Aerobic microbial degradation of PCP results in transformation to the ultimate metabolites, carbon dioxide and chloride ion, as shown in Figure 2 (Crosby 1981). Watanabe (1973) isolated a PCP-decomposing Pseudomonas from treated soil. Pseudomonas degraded PCP and released carbon dioxide and the intermediate metabolites (tetrachlorocatechol and tetrachlorohydroquinone). Pentachlorophenol has been reported to be converted into pentachloroanisole and tetrachlorohydroquinone dimethyl ether by a Bacillus sp. (Kirsch and Etzel 1973). Several species of fungi also depleted PCP from PCP-treated wood blocks (Duncan and Deverall 1964). Slow chloride release and detoxication of PCP occurred employing the fungal enzymes laccase, tyrosinase, and peroxidase. Cserjesi (1972) found that PCP


OH
OH
OX
OCH$_3$
OCH$_3$
OH
OH
1,4
OH
2,3,4
1,2,4
1,3
1,3
OCH$_3$
1,2,4
1
OH
OH
1
1,2
2
OX
OH
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OCH$_3$
Cl$_4$
OH
Cl$_3$
1
1
1
OCH$_3$
Cl$_3$
OH
Cl
1
CO$_2$, Cl$^-$
1
OCH$_3$
Cl

Figure 2. Biodegradation of PCP. For clarity, Cl substituents are indicated only by lines. 1 = Microorganisms, 2 = Mammals, 3 = Fish and aquatic invertebrates, 4 = Green plants (Crosby 1981).

disappeared during a 12 day incubation with cultures of fungus Trichoderma. The fungus was shown to methylate PCP to pentachloroanisole. Similarly, several fungal species also caused methylation of tetrachlorophenol to tetrachloroanisole.

Ability to degrade PCP may not be uniform among microorganisms. No degradation of PCP was found in a mixed population grown from a soil suspension (Alexander and Aleem 1961); likewise, no degradation was observed in acclimated activated sludge (Ingols et al. 1966). However, PCP was found to be readily biodegradable in water from an activated sludge plant (Kirsch and Etzel 1973). Adaptation of microbial populations to PCP (along with the control of pH) may play an important role in the degradation.

A summary of PCP degradation studies is presented in Table 12. Degradation half-lives for aerobic soil treatment systems ranged from greater than 30 days for nonacclimated systems to less than 1 day for fully acclimated or inoculated systems. Most studies used initial PCP concentrations of from 10 to 30 mg/kg of soil, dry weight. However, one long-term study by McGinnis indicated that PCP concentrations of over 2,000 mg/kg soil could be rapidly and completely degraded by a well-acclimated soil treatment system (McGinnis 1985).

Immobilization of PCP--

The degree of adsorption of PCP affects both its rate of degradation and its tendency to disperse by leaching. PCP is, in general, more mobile in high pH soils than in acidic soils (Choi and Aomine 1973, 1974a; Green and Young 1970, Nose 1966). At alkaline pH, PCP exists as the dissociated anion, which is highly water soluble and is not easily adsorbed to soils having a net negative charge.

In a study by Choi and Aomine (1974a) using 13 soil samples with various clay mineral species, organic matter content, and pH, "apparent adsorption" (defined as the amount of PCP that disappeared from the liquid phase of the soil/PCP system) was the greatest in the strong acid soil system compared to the moderate acid soil system, regardless of the species of clay mineral or organic matter content. No adsorption occurred in the slightly acid or neutral soil system. Organic matter was also important in PCP adsorption, since soils higher in organic matter showed a greater adsorption of PCP than soils lower in organic matter. "Apparent adsorption" was shown to include both the mechanisms of adsorption or soil colloids and precipitation in the soil micelle and in the external liquid phase, depending on the soil pH (Choi and Aomine 1974b).

Piontek (1984) conducted a study to determine the adsorption of PCP onto soils at concentrations that are of concern in groundwater pollution, i.e., in the part per billion range. Results of the study again showed that, although organic matter content of a soil is important in determining the extent of adsorption of PCP, an even more important soil property is pH. Adsorption of PCP significantly increased with decreased pH. The adsorption coefficients obtained in the batch adsorption experiments indicated significant retardation of PCP. However, the adsorption was shown to be reversible. Therefore, PCP may not be permanently immobilized in the soil phase, but may be slowly released as water with lower concentration of PCP moves through the soil.

TABLE 12. SUMMARY OF BENCH AND PILOT SCALE PCP DEGRADATION STUDIES (ERT, INC. 1985a)

Scale	Temperature (°C)	Soil pH	% Soil Moisture Content	Average Initial Concentration (mg/kg dry soil)	Microbial Conditions	Degradation Rate	Reference
Pilot (4'x4' test plots)	8-16	6.7	15	30	Not acclimated, Aerobic	25% after 12 days	Edgehill and Finn (1983)
Pilot (4'x4' test plots)	8-16	6.7	15	30	Inoculated, Aerobic	Half-life 6 days	Edgehill and Finn (1983)
Bench (10 g soil)	23	7.1	16	10	Not acclimated,	80% after 160 days	Baker and Mayfield (1980)
Bench (10 g soil)	23	7.1	16	10	Not acclimated, Anaerobic	7% after 160 days	Baker and Mayfield (1980)
Bench	30	6.7	15 to 20	20	Not acclimated, Aerobic	Half-life 12 to 14 days	Edgehill and Finn (1983)
Bench	30	6.7	15 to 20	20	Inoculated, Aerobic	90% in 24 to 100 hours[1] (Half-life ~ day)	Edgehill and Finn (1983)
	0	-	-	-	Not acclimated, Aerobic	24% in 30 days	Baker, Mayfield and Inniss (1980)
	20	-	-	-	Not acclimated, Aerobic	29% in 30 days	
Bench (40 g soil)	31	7.0		2250[2]	Acclimated for 1 year, Aerobic	Half-life 21 hrs	McGinnis (1985)

[1] 90 percent degradation achieved in 24, 40, and 100 hours with inoculum concentrations of 10^6, 10^5, and 10^4 cells per gram of soil, respectively.

[2] Assumes 15 percent soil moisture content.

Photodecomposition of PCP--

Photodecomposition may be an important route whereby a chemical is eliminated from the environment. PCP undergoes various reactions while it absorbs light energy (the long-wave absorption maxima lie near 300 nm in organic solvents or below pH 5 (Crosby 1981)). In organic solvents or in water, PCP is photochemically reduced to isometric tri- and tetrachlorophenols (Crosby and Hamadmad 1971). Nucleophiles such as bromide ion can displace chloride from the excited PCP ring and in an aqueous solution exposed to sunlight, PCP undergoes the replacement of ring chlorines by hydroxyl groups. The resulting products are oxidized by air to quinones, which subsequently are dechlorinated (Crosby and Wong 1976).

Pignatello et al. (1983) showed that in an aquatic system, photolysis accounted for 5 to 28 percent decline in initial PCP concentrations. Photolysis was rapid at the water surface but greatly attenuated with depth. Lamparski et al. (1980) demonstrated that PCP could undergo photolytic condensation reactions to form octachlorodibenzo-p-dioxin on a wood substrate. This effect was greatly reduced by the addition of a hydrocarbon oil.

Volatilization of PCP--

The volatility of PCP from a soil system is dependent on the soil pH. In general, volatilization of PCP is not expected to be significant from land treatment soil systems. PCP is relatively volatile but Na-PCP is nonvolatile (Crosby 1981). Therefore, as soil pH is raised above the PCP pKa of 4.7, volatility decreases because the ionized form of PCP is predominant at pH levels that are optimum for biological treatment of added organic wastes, i.e., pH of 6 to 7 (Luthy 1984).

Bioaccumulation of PCP--

Bioaccumulation of PCP from water, like toxicity, has been shown to be inversely related to pH (U.S. EPA 1986a). PCP bioconcentrated in the tissues of fish from 7.3 to 1,066 times with test durations from 16 to 115 days. The gall bladder concentrated the highest levels of PCP, whereas muscle and skin contained the lowest concentrations of PCP in rainbow trout exposed to 0.78 to 1.15 μg/L (U.S. EPA 1986a).

In general, bioaccumulation of PCP has been found to be short-term because organisms tend to metabolize and excrete these compounds (Versar 1979). Residues of PCP in fish have been shown to drop quite rapidly upon termination of exposure (U.S. EPA 1986a). Ninety-six percent of whole body ^{14}C-labelled PCP was eliminated by fathead minnows within 3.5 days, while about 85 percent of the PCP residues in bluegill muscle were eliminated in 4 days. A first-order simulation model developed from empirical data indicated a half-life of 2.7 days in rainbow trout, with 95 percent elimination in 11.7 days.

Little information exists on plant metabolism of PCP, although PCP is very phytotoxic (Crosby 1981). Studies were performed on application of radio-labelled PCP to cotton plants (Miller and Aboul-Ela 1969). The kernels of bolls, which were closed at spraying time, contained residues of radioactivity. Application of PCP to sugar cane leaves resulted in almost complete recovery of the PCP from the leaves, while root application deposited most of the compound in the roots (Hilton et al. 1970). Studies on the growth of rice in soil treated with radio-labelled PCP showed that after one week, the plants had absorbed about 3 percent of the applied radioactivity (Haque et al. 1978).

PETROLEUM REFINING INDUSTRY

Introduction

There are approximately 250-300 petroleum refineries in the United States. These refineries vary from complex plants producing a variety of petroleum products and petrochemical feedstock to simple plants producing only a small number of products (ERT 1984). The six major groups of operations and processes in a petroleum refinery are: 1) storage of crude oil intermediates and final products; 2) fractionation such as distillative separation and vacuum fractionation; 3) decomposition such as thermal cracking, catalytic cracking, and hydrocracking; 4) hydrocarbon rebuilding and rearrangement such as polymerization, alkylation, reforming, and isomerization; 5) extraction such as solvent refining and solvent dewaxing; and 6) product finishing such as drying and sweetening, lube oil finishing, blending, and packing (Hornick et al. 1983).

Waste Characteristics

Crude oil is the raw feedstock for all of the refinery process operations. Portions of the crude oil and the refined products are eventually discharged as wastes, either directly from a refinery process or to the wastewater treatment plant (ERT 1984).

Those refinery wastes known to be land treated are listed in Table 13. Of the listed wastes, five contribute over 90 percent of the estimated oil and solids content applied to land treatment facilities. These wastes include API separator sludge (K051), dissolved air flotation float (K048), slop oil emulsion solids (K049), wastewater treatment sludge (nonlisted), and nonleaded tank bottoms (nonlisted).

The two waste streams investigated for land treatment potential in this study were API separator sludge (K051) and slop oil emulsion solids (K049). API separator sludge is the sludge generated in the oil/water/solids (API) separator. API separators are usually connected to the refinery oily water sewer. Slop oil emulsion solids are the residuals left in the emulsion layer after treatment in the slop oil tank, i.e., the emulsion that cannot be broken.

Refinery wastes vary considerably in physical composition, depending upon the petroleum product being produced and according to waste type, as shown in Table 14. Overcash and Pal (1979) summarized the chemical composition of 12 API refinery wastes (Table 15).

TABLE 13. REFINERY WASTES KNOWN TO BE LAND TREATED AND RELATIVE PERCENTAGES OF EACH WASTE WHICH ARE LAND TREATED (ERT 1984)

Waste Category	Listed* Hazardous Waste	Hazardous* Waste Number	Known To Be Land Treated?	Residue from Wastewater Treatment Process	Estimated % Each Waste Constitutes of Totals which are Land Treated: Oil Basis	Estimated % Each Waste Constitutes of Totals which are Land Treated: Oil and Solids Basis
Dissolved Air Flotation Float	Yes	K048	Yes	Yes	18.68	12.66
API Separator Sludge	Yes	K051	Yes	Yes	40.32	36.46
Slop Oil Emulsion Solids	Yes	K049	Yes	Yes	14.57	9.24
Heat Exchange Bundle Cleaning Sludge	Yes	K050	Yes	Yes	0.01	0.08
Tank Bottoms (leaded products)	Yes	K052	Yes	No	0.09	0.19
Wastewater Treatment Sludge	No		Yes	Yes	7.18	17.11
Storm Water Runoff Silt	No		Yes	Yes	N.D.	N.D.
Spent Filter Clays	No		Yes	No	0.36	
Tank Bottoms+ (nonleaded products)	No		Yes	No	18.35	17.70
Fluid Catalytic Cracking Catalyst Fines	No		Yes	No	0.05	2.06
Spent Catalysts	No		Yes	No	0.01	0.61
Cooling Tower Sludges#	No		Yes	Yes	0.04	1.22
Chemical Precipitation Sludges	No			Yes	N.D.	N.D.
Neutralized HF Alkylation Sludge	No		Yes		0.30	1.81

*40 CFR 261.

+Includes crudes intermediates and product storage tanks.

#Includes once through cooling waters sludge.

N.D. - No Data.

TABLE 14. PHYSICAL COMPOSITION OF REFINERY WASTES (ENGINEERING SCIENCE 1976)

Waste Type	Typical Composition, Percent		
	Oil or Hydrocarbon	Water	Solids
API Separator	8	73	19
Tank Bottoms	60	37	3
Air Flotation Froth	7	88	5
Biological Treatment Sludges	3	92	5
Cooling Tower Sludge	1	74	25
Spent Treatment Clay	17	9	74
Waste Lime Sludge	0	73	27

TABLE 15. COMPOSITION OF 12 API REFINERY WASTES (OVERCASH AND PAL 1979)

	Minimum	Maximum	Average
Sulfides (mg/l)	1.3	38	8.8
Phenol (mg/l)	7.6	61	27
BOD (mg/l)	97	280	160
COD (mg/l)	140	640	320
pH	7.1	9.5	8.4
Oil (mg/l)	23	130	57

ERT, Inc. (1984) conducted a literature review of Appendix VIII constituents that may be present in petroleum wastes for the American Petroleum Institute. They identified three general classes of constituents: 1) Appendix VIII constituents known to be present; 2) Appendix VIII constituents suspected to be present; and 3) Appendix VIII constituents expected not be present. The results of these investigations are shown in Table 16. The U.S. EPA has defined a list of Appendix VIII compounds expected to be present in petroleum refinery wastes; this list is presented in Table 17.

Treatment of Petroleum Refinery Wastes in Soil Systems--

The petroleum industry has documented its experience with land-farming in the open literature more extensively than most others (Corey 1982). The technique is preferred by the industry for the management of waste sludges and petroleum-containing solutions because of the minimum energy required for implementation and operation. The industry has considered and obtained data on decomposition rate, vegetative response, odor, and flammability.

TABLE 16. CATEGORIES FOR APPENDIX VIII CONSTITUENTS IN REFINERY WASTES WHICH ARE LAND TREATED[*] (ERT, INC. 1984)

Known to be Present	Suspected to be Present	Expected not to be Present
Arsenic	Anthracene	All other EPA Appendix VIII Constituents
Benzene	Antimony	
Bis(2-ethylhexyl)phthalate	Barium	
Butyl benzyl phthalate	Benz(c)acridine	
Benz(a)anthracene	Benzo(b)fluoranthrene	
Benzo(a)pyrene	Benzo(j)fluoranthrene	
Benzo(k)fluoranthrene	Cobalt	
Beryllium	Dibenz(a,h)acridine	
Cadmium	Dibenz(a,j)acridine	
Chromium	Dibenz(a,h)anthracene	
Chrysene	Dibenz(c,g)carbazole	
Copper[+]	Dibenz(a,e)pyrene	
Cyanide	Dibenz(a,h)pyrene	
Fluoranthene	Dibenz(a,i)pyrene	
Lead	Diethyl phthalate	
Mercury	Dimethyl phthalate	
Naphthalene	Ethylene dibromide	
Nickel	Ethylene dichloride	
Phenol	7,12-dimethylbenz(a)anthracene	
Selenium	2,4-dimethyl phenol	
Toluene	4,6-dinitro-o-cresol	
Vanadium	2,4-dinitrotoluene	
Zinc[+]	2,6-dinitrotoluene	
	2,4-dinitrophenol	
	di-n-butylphthalate	
	di-n-octylphthalate	
	2-methyl naphthalene	
	Hydrogen sulfide	
	Indeno(1,2,3-cd)pyrene	
	Nitrobenzene	
	4-nitrophenol	
	P-cresol	
	Phenanthrene	
	Tetraethyl Lead	

[*] A list of constituents suspected to be present is currently being developed by EPA as of 5/84.

[+] Non-Appendix VIII constituents.

TABLE 17. CONSTITUENTS OF PETROLEUM REFINING WASTES (AS APPROVED BY U.S. EPA)

Metals

Antimony
Arsenic
Barium
Beryllium
Cadmium
Chromium
Cobalt
Lead
Mercury
Nickel
Selenium
Vanadium

Volatiles

Benzene
Carbon disulfide
Chlorobenzene
Chloroform
1,2-Dichloroethane
1,4-Dioxane
Ethyl benzene
Ethylene dibromide
Methyl ethyl ketone
Styrene
Toluene
Xylene

Semivolatile Base/Neutral Extractable Compounds

Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Chrysene
Dibenz(a,h)acridine
Dibenz(a,h)anthracene
Dichlorobenzenes
Diethyl phthalate
7,12-Dimethylbenz(a)anthracene
Dimethyl phthalate
Di(n)butyl phthalate
Di(n)octyl phthalate
Fluoranthene
Indene
Methyl chrysene
1-Methyl naphthalene
Naphthalene
Phenanthrene
Pyrene
Pyridine
Quinoline

Semivolatile Acid-Extractable Compounds

Benzenethiol
Cresols
2,4-Dimethylphenol
2,4-Dinitrophenol
4-Nitrophenol
Phenol

Application rates generally range from less than 200 barrels/year/acre to more than 600 barrels/year/acre. The frequency of application of oily wastes varies widely from only one application per year to a site to multiple applications as frequently as once per week. The decomposition rate is site specific but has been reported as high as 50 percent per year (Corey 1982). Subsurface samples indicate that if land treatment units are operated correctly, neither heavy metals nor oil will migrate appreciably. Trace metal analysis of vegetation growing on oiled areas is generally similar to control locations. Odor is reduced and minimal once the oily waste is blended with the soil. After the wastes are mixed with the soil they are generally not flammable. A review of land treatment of refinery wastes, *Sludge Farming: A Technique for the Disposal of Oil Refinery Wastes* (CONCAWE 1980) was prepared by the Oil Companies' International Study Group for Conservation of Clean Air and Water-Europe to evaluate the potential for land treatment of refinery wastes in Europe. CONCAWE concluded that, provided simple safeguards are observed, sludge farming is ecologically the most suitable and cost effective method for disposal of normal oil sludges and for soil that has been accidentally contaminated with oil.

PAH compounds are important constituents in petroleum refinery wastes (Tables 16 and 17) as well as in wood preserving wastes, and the reader is referred to the discussion of the fate and significance of PAHs in soil systems presented previously for wood preserving wastes.

Toxicological Significance of Petroleum Wastes--

API separator sludge/slop oil emulsion solids and oil-containing storm water runoff have been shown to contain mutagenic compounds (Donnelly et al. 1985). Organic compounds were extracted from each waste with dichloromethane and partitioned by liquid-liquid extraction into acid, base, and neutral fractions. A battery of short term bioassays were used to detect various types of genotoxic damage. Each chemical fraction was tested in four strains of *Salmonella typhimurium* to detect point mutations, six strains of *Bacillus subtilis* to detect lethal damage to DNA, and haploid and diploid forms of *Aspergillus nidulans* to detect point mutations and various types of chromosome damage. Results of these biological analyses indicated the presence of genotoxic compounds in all three fractions of each waste.

Brown and Donnelly (1984) conducted a study of the mutagenic potential of runoff and leachate water from petroleum API separator sludge-amended soils, using the *Salmonella* microsome assay and the *Bacillus subtilis* DNA repair assay. Mutagenic activity was detected in a limited number of runoff and leachate samples, but greater amounts of mutagenic activity were detected in the runoff water. The mutagenic activity from leachate and runoff water decreased with time following waste application in two of the three soils used. The activity in the third soil did not decrease over the 3 years of observation.

The toxicity of petroleum refinery effluents to environmental organisms is highly dependent upon the waste streams, which may vary widely in chemical composition. Data suggest that many effluents, especially those that have received primary treatment only, are toxic at their discharge point (CONCAWE 1979). CONCAWE (1979) summarized the environmental toxicological effects of petroleum refinery effluents and found that in general, oils increase in toxicity with levels of low-boiling compounds, unsaturated compounds, and aromatics. Also aromatics with increased numbers of alkyl substituents have higher toxicities, and toxicity increases along the series alkanes-alkenes-aromatics. Cycloalkanes and cycloalkenes appear to be more toxic than alkanes.

Other components of petroleum refinery effluents, such as phenols, sulfur compounds, cyanides, and metals may also contribute to the toxicity of the effluent. A review of the toxicity of these compounds as well as the toxicity of oils is presented in a report prepared for the Council of European Communities by CONCAWE's Water Pollution Special Task Force No. 8 (CONCAWE 1979).

Human health effects of specific compounds often found in petroleum refinery effluents may be found in the U.S. EPA Health Effects Assessment documents for PAHs (U.S. EPA 1984e), benzo(a)pyrene, (U.S. EPA 1984b), and coal tars (U.S. EPA 1984c).

Degradation, Transformation, and Immobilization of Petroleum Refinery Wastes--

A summary of land treatment practices in the petroleum industry was published by API (API 1983). Results of this study showed high oil removal efficiencies for the 14 full scale and 4 pilot scale facilities reviewed. Oil reductions at the full scale facilities ranged from 0.09 - 0.86 lb of oil/ft^3/degradation month and were directly related to the oil loading rates, which ranged from 0.16 to 1.12 lbs of oil/ft^3/degradation month. Slowly degradable fractions were retained within the zone of incorporation. The saturate and light aromatic fractions degraded at a faster rate than the heavier fractions. Lead and chromium accumulated above background in the surface soils at some of the land treatment facilities investigated. The metals were attenuated with depth and rarely moved beyond the zone of incorporation, generally reaching background concentrations within 1 to 3 feet below the zone of incorporation.

Martin and Sims (1984) and Martin et al. (1986) investigated land treatment practices in the petroleum refining industry. Sites for land treatment were characterized by a variety of climate, soil, and physical characteristics that were suitable for land treatment. Maximum waste application rates ranged from 0.004 weight percent of oil in soil per application to 8 percent per application. Five facilities were identified as practicing high intensity land treatment (defined as a minimum of 4.0 percent oil/soil for climatic regions where seasonal fluctuations cause the average minimum air temperature to fall below 9.9°C, and 8.0 percent oil/soil for climatic regions where the average minimum air temperature is greater than or equal to 9.9°C). Seventy percent of the facilities added amendments (fertilizer and lime) to the treatment soil. Calculations using a predicted half-life of 304 days for oil in soil showed that expected maximum weight percentage of oil in the soil after treatment ranged between 2.9 percent and 19 percent, with an average of 7.9 percent. Calculations to predict the total inorganic constituent loading over a projected 30 year site life indicated that levels would be below suggested limits (U.S. EPA 1983).

Pal and Overcash (1980), using available data on petroleum refinery solid wastes, performed an assessment of land treatment technology for these wastes. Using two representative soil types and the composite waste characterization shown in Table 18, the land-limiting waste constituent (LLC) (i.e., that waste constituent requiring the largest land area for assimilation in the soil system) was determined to be fluoride. Elimination of one waste stream, the neutralized HF alkylation sludge, from the land treatment unit eliminated nearly all of the fluoride, and selenium, chromium, and spent filter clay became the LLCs.

The addition of oily wastes to a soil may change its chemical, biological and physical properties. Initially, oil applications tend to produce a hydrophobic effect in soil, resulting in a decreased infiltration rate. This effect is due to the oil itself and to the accumulation of hydrophobic mucilaginous substances generated by increased microbial growth (Overcash and Pal 1979). Long-term effects of the applied oil may be beneficial. Aggregation, soil porosity, and water holding capacity all increase while bulk density decreases (Hornick et al. 1983).

As the oil content of the soil decreases at a land treatment facility, there is an increase in heavy aromatics and asphaltenes compared to the saturates and light aromatic hydrocarbon fraction of the applied oil (Huddleston and Creswell 1976). The heavy aromatics and asphaltenes do appear to degrade but at much slower rates than the overall oil reduction rate (Weldon 1982). Table 19 shows the relative order of resistance of hydrocarbons to biodegradation, as reported by Fredericks (1966). Perry and Cerniglia (1973) reported that the recalcitrance of various hydrocarbon substrated increased in the following order: normal alkanes C_{10} - C_{19}; straight-chain alkanes C_{12} - C_{18}; gases C_2 - C_4; alkanes C_5 - C_9; branched alkanes to 12 carbons; alkenes C_3 - C_{11}; branched alkenes; aromatics; and cycloalkanes.

Brown et al. (1981) conducted a study of degradation of API separator sludge from a petroleum refinery in four different soils at four moisture levels. The greatest amount of degradation was seen in a sandy clay soil, intermediate amounts in a clay and a sandy loam soil, and the least in a clay soil. In the sandy clay soil, the biodegradation rate generally doubled between 10° and 30°C but decreased at 40°C. At 30°C, after 180 days, 45 percent of the refinery waste (measured as total carbon or residual hydrocarbon) was degraded, but at 40°C, after 180 days, only 36 percent was degraded. Addition of fertilizer nutrients (nitrogen, phosphorus, and potassium) did not increase biodegradation. Biodegradation rate increased with increased application rates of the sludge. Moisture was a dominant factor only at excessively wet or dry conditions. Moisture content had a greater influence on biodegradation at 10°C than at higher temperatures.

Dibble and Bartha (1979) investigated the effects of environmental parameters on the biodegradation of oil sludge (as measured by CO_2 evolution and analysis of hydrocarbons) in a loam soil. The environmental parameters investigated included incubation temperature, pH, soil moisture, waste application rate and frequency, and the addition of mineral nutrients, micronutrients and organic supplements (sewage sludge). They concluded that oil sludge biodegradation was optimal at a soil water holding capacity of 30-90 percent, a pH of 7.5 to 7.8, C:N and C:P ratios of 60:1 and 800:1,

TABLE 18. WASTE CHARACTERIZATION FOR AGGREGATE OF SIXTEEN SOLID WASTE STREAMS FROM A CATEGORY IV PETROLEUM REFINERY (PAL AND OVERCASH 1980)

Parameter	Concentration*, mg/l	Parameter	Concentration*, mg/l
Total Solids (TS)	500,000	Manganese (Mn)	42
Oil	71,000	Cobalt (Co)	1.8
Nitrogen (N)	200	Nickel (Ni)	14
Phosphorus (P)	110	Zinc (Zn)	53
Potassium (K)	40	Silver (Ag)	0.35
Calcium (Ca)	300	Cadmium (Cd)	0.17
Sodium (Na)	200	Lead (Pb)	9.3
Magnesium (Mg)	80	Molybdenum	1.3
Cyanide (CN)	0.67	Boron	0.015
Phenol	3.6	Fluoride	530
Selenium (Se)	1	Chloride	99
Arsenic (As)	1.3	Benz[a]pyrene	0.08
Mercury (Hg)	0.26	Spent Filter Clay	70,000
Beryllium (Be)	0.06	pH (S.U.)	6.5 - 8.2
Vanadium (V)	15.3	Chemical Oxygen Demand	130,000
Chromium (Cr)	58	Volume	15×10^6 ℓ

*Wet sludge basis.

TABLE 19. RELATIVE RESISTANCE OF HYDROCARBONS TO BIOLOGICAL OXIDATION (FREDERICKS 1966)

Most Readily Oxidized Biologically

↓

Class I

n-paraffins C_9 to C_{18}

Class II

branched alkanes with preference for homologues

1) 3-methylpentane
2) 2,2,4-trimethylpentane
3) pentamethylpentane
4) 2,2,4,4,6,8,8-heptamethylnonene

Class III

n-paraffins C_5 to C_8

Class IV

cyclic hydrocarbons (alicyclics oxidized more readily than aromatics)

1) cyclohexane
2) methylcyclohexane
3) decalin
4) benzene
5) m-xylene

Most Resistant to Microbial Oxidation

respectively, and a temperature of 20°C or above. The addition of micronutrients and organic supplements in the form of sewage sludge did not enhance biodegradation. The sewage sludge inhibited hydrocarbon biodegradation. Breakdown of the saturated hydrocarbon (alkane and cycloalkane) fraction was the highest at low application rates, but higher application rates enhanced biodegradation of the aromatic and asphaltic fractions. Frequent small applications (four small loadings) resulted in higher biodegradation rates and total hydrocarbon biodegradation than a single large application. The authors suggested that a loading rate of two 100,000 liters/hectare or four 50,000 liters/hectare oil sludge hydrocarbon applications per growing season may be appropriate for most temperate zone disposal sites.

Kincannon (1972) conducted a study of degradation of three types of oily sludges in a sandy clay loam soil. The wastes were applied to plots that had been previously used for oily waste disposal. Residual oil levels before the beginning of the study were about 10 percent, and nitrogen and phosphorus were added as amendments. Degradation rates ranged from 0.167 to 1.79 pounds of oil per month per cubic feet of soil. For crude oil tank bottoms (containing a variety of hydrocarbon types) and a high molecular weight fuel oil (containing olefinic and aromatic compounds), both aromatic and saturated hydrocarbons were reduced through time, but for the waxy raffinate sludge (containing highly paraffinic components), only the saturate fraction was reduced. The optimum fertilization program was determined as the maintenance of 10-50 ppm ammonium and/or nitrate and a slight excess level of potassium and phosphorus in the soil. The major species of microorganisms degrading the hydrocarbon substrate were the genera Pseudomonas, Flavobacterium, Nocardia, Corynebacterium, and Arthrobacter. Neither the type of oil sludge, temperature or addition of fertilizer affected the types of organisms present, though both the type of sludge and fertilizer affected the total number of aerobic bacteria present in the soil.

Meyers and Huddleston (1979) investigated the degradation of a combined oily sludge consisting of API separator sludge, tank bottoms, and slop oil at a land-farm. Three applications were studied in plots with and without vegetative cover: a single loading, loading one time each year for 2 years, and loading one time each year for 3 years. Agricultural ammonium nitrate and phosphate were added to all test plots. Selected results of the study are shown in Table 20. All three oil fractions were shown to degrade. Also, tilling was shown to increase biodegradation, likely due to increased aeration and microbial/oil contact.

A 1,280-day laboratory simulation of the "landfarming" process by Bossert et al. (1984) explored the fate in soil of PAHs and total extractable hydrocarbon residues originating from the disposal of an oily sludge. In addition to the measurement of CO_2 evolution, periodic analysis of PAHs and hydrocarbons monitored biodegradation activity. The estimation of carbon balance and of soil organic matter assessed the fate of residual hydrocarbons. Seven sludge applications during a 920-day active disposal period were followed by a 360-day inactive "closure" period with no further sludge applications. A burst of CO_2 evolution followed each sludge addition, but substantial amounts of undegraded hydrocarbons remained at the end of the study. Hydrocarbon accumulation did not inhibit biodegradation performance. Conversion of hydrocarbons to CO_2 predominated during active disposal;

incorporation into soil organic matter predominated during the closure period. In this sludge, the predominant PAHs were degraded more completely (85 percent) than total hydrocarbons. Both biodegradation and abiotic losses of three- and four-ring PAHs contributed to this result. Some PAHs with five and six rings were more persistent, but these constituted only a small portion of the PAHs in the sludge.

TABLE 20. RESULTS OF DEGRADATION OF PETROLEUM WASTES AT A LAND-FARM AFTER 25 MONTHS (MEYERS AND HUDDLESTON 1979)

Plot	Degradation (%)			
	Oil	Paraffins	Aromatic	Resins and Asphaltenes
Single loading, No Vegetative Cover	58	71	47	37
Two Yearly Loadings, No Vegetative Cover	30	44	29	12
Two Yearly Loadings, Vegetative Cover of Wheat and Bermuda Grass	43	50	44	30

Snyder et al. (1976) studied the disposal of waste oil re-refining residues by land farming. The residues consisted of a sludge and an oil-water emulsion (approximately 60-65 percent water) containing various metals at concentrations of 3 - 400 μg/g. For the plots treated with oil, the microbial respiration rates were much higher than for the untreated plots.

Snyder et al. (1976), Skujins and McDonald (1983), and Skujins et al. (1983) reported on the degradation of waste oil in a semi-arid region soil near the Great Salt Lake, Utah. An oil emulsion (45.7 percent oil) and a water phase (formed in a waste oil lagoon between the surface oil emulsion layer and the bottom sludge sediment) were treated by a land-farming method employing neutralization of the waste and supplemental fertilization. By the end of the first year following the application of the oily waste, the mean value of oil degradation was 37 percent. During the second, third and fourth years, 81, 84, and 91 percent, respectively, of the added oil was degraded (Skujins and McDonald 1983). There was no significant difference in degradation rates among the various treatments with respect to the amount of oil and nitrogen fertilizer (i.e., the C/N ratio) applied to the soil. Maximum rates of degradation occurred during the moist, warm spring seasons. The area was successfully revegetated, but the plants contained elevated levels of metals in comparison to plants from control areas (Skujins et al. 1983). The investigators suggested that reuse of the disposal area may be limited by increased metal availability to plants.

A study by Westlake et al. (1977) of the degradation of refined oil in a fertilized soil of the boreal region of the Northwest Territories, Canada showed that the addition of oil-utilizing bacteria to soil plots did not increase the number of bacteria present compared to plots not seeded with oil-utilizing bacteria. All plots that received an application of oil and fertilizers with or without bacterial seeding showed a two-log increase in the number of viable bacteria present within 22 days of the initiation of the experiment. The high bacterial numbers persisted for almost three years before decreasing to levels present in unfertilized oil-soaked plots. Little change was noted in the aromatic contents of both fertilized and unfertilized plots, but the n-alkane components of the saturate hydrocarbon fractions were shown to be degradable in the fertilized plots.

An industrial oily waste was applied to field plots in New York to determine the degradation and immobilization of waste constituents and to determine the impact of the wastes on soil biota (Loehr et al. 1985). Wastes were applied three times to the test plots at loading rates ranging from 0.17 to 0.5 kg oil/m^2 or from 0.09 wt percent - 5.25 wt percent oil in soil. The waste application increased soil pH and volatile materials. Half-lives of the oil ranged from 260 to 400 days. Refractory fractions of the applied oil ranged from 20 to 50 percent, but did not appear to adversely affect soil biota. Naphthalenes, alkanes, and specific aromatics were lost rapidly, especially in the warmer months, with half lives generally less than 30 days. The waste applications reduced numbers and biomass of earthworms and numbers and kinds of microarthropods, but both types of biota were able to recover. Earthworms did not accumulate specific waste organic compounds.

Results at pilot scale facilities have shown that accumulated oil continues to degrade for several years after oil applications have terminated and the land treatment facility is closed, even with no efforts to enhance degradation (Weldon 1982). A 50 percent reduction in soil oil concentration was observed over 2-year periods at closed pilot scale facilities that had oil concentrations in the soil greater than 3 percent at the time of closure.

A 15-month closure evaluation study was performed for three land treatment sites that had ceased application of refinery wastes for 6 months, 9 months, and 6 years (Streebin et al. 1984). Considerable variation in oil content existed among the three sites. Concentrations of oil greater than background levels were found as deep as 45-50 cm at all three sites. Average oil content remained relatively constant throughout the study, perhaps due to long periods of wet or dry soil, low soil nitrogen, and presence of persistent hydrocarbons. Only traces of organic priority pollutants were found below the zone of incorporation. Metals were fixed and/or sorbed in the top 25 cm of soil at all sites.

A study of the distribution of inorganic constituents in soil following land treatment of refinery wastes at five sites was conducted by Brown et al. (1985). At one site, where soil pH was less than 6.5, two metals, chromium and lead, were found below the zone of incorporation at concentrations above untreated soil. Metal levels within the zone of incorporation at all sites were at levels considered common for natural soils. A wide variation in oil content in the zone of incorporation was noted, i.e., from 3.4 percent to 8 percent (K.W. Brown and Associates 1981). The oil content below the zone of incorporation decreased rapidly with depth. The maximum extent of oil migration for the facilities reviewed was less than 1.5 feet below the zone of incorporation.

Volatilization of Petroleum Refinery Wastes--

Dupont (1986b) evaluated volatile air emissions from land treatment systems using API separator sludge and slop oil emulsion solids applied to laboratory soil microcosms. Data indicate that vapor partitioning and retardation by soil organic matter were of minor importance in vapor soil transport processes, and that volatile organic vapor soil diffusion could be described by the physical environment through which the vapor travels. Using an air emission predictive model (the Thibodeaux-Hwang AERR model (Thibodeaux and Hwang 1982)), subsurface waste application produced a two- to ten-fold decrease in predicted emission rates compared to surface application. This reduced emission rate persisted for the 80 to 100 hours over which the experimental runs were conducted.

Radian Corporation (Wetherold and Balfour 1986) has also conducted studies to evaluate air emissions from land treatment of oily sludges. The studies included laboratory land treatment simulation experiments, field studies at a waste treatment facility, and field studies at a refinery land treatment site. Results of these studies include: emission rates reach their maximum in a relatively short time after surface application of a volatile sludge; the most significant parameters affecting the emission rate from surface applications of sludge are the loading and the sludge volatility; the Thibodeaux-Hwang emission model appears to agree reasonably well with the measured rates for some selected compounds; the Thibodeaux-Hwang emission model has not been generally applicable to multicomponent mixtures, probably because of the uncertainty in defining accurate multicomponent parameters for use in the model; during land treatment a significant fraction of the applied VOC is emitted from the surface application of oily sludge; tilling causes a significant, short-term increase in the VOC emission rate from land treatment sites. API (1983) has suggested that subsurface injection may be used to reduce volatile air emissions if tilling does not occur within four to six days of application.

A description of the flux chamber/solid sorbent monitoring system used to evaluate air emissions from land treatment facilities was presented by Dupont (1986a).

SECTION 5

RESULTS AND DISCUSSION

QUALITY ASSURANCE/QUALITY CONTROL

A quality assurance (QA) project plan was developed by the Utah Water Research Laboratory (UWRL), approved by the U.S. EPA, and implemented by the UWRL to ensure that data generated in this research investigation were of adequate quality and quantity to support the conclusions being drawn from the study. Key elements of this plan included the following activities during the performance of the project:

(1) Use of U.S. EPA-approved or other standard methodology for analytical measurements and sample preservation and collection

(2) Documentation of modifications of standard procedures

(3) Thorough description of experimental procedures

(4) Use of replicate analyses and positive and negative controls for experimental and analytical procedures

(5) Analysis of subsamples of selected samples

(6) Use of U.S. EPA quality assurance audit samples

(7) Calculation of mean values, standard deviations, and coefficients of variation

(8) Use of statistical procedures for evaluation and interpretation of data

(9) Use of standardized data collection formats and reporting, including the use of bound laboratory notebooks

(10) Periodic maintenance and calibration of laboratory instrumentation

(11) Participation in U.S. EPA performance evaluation study

(12) Systems audit by U.S. EPA RSKERL QA project officer (i.e., a qualitative, on-site review to ensure that data are being collected in accordance with the QA project plan).

Descriptions of quality control (QC) activities for specific experimental and analytical procedures are included with the description of the procedure in this report, or in the referenced procedure. Results of QC activities are included with presentations of results for specific experimental studies and analytical measurements.

WASTE CHARACTERIZATION

Introduction

Demonstration of the land treatability of a waste begins with waste characterization. A waste characterization scheme should delineate the various waste components that must be managed to preclude adverse health, safety, or environmental impact from land treatment of a given hazardous waste. Characterization provides the basis both for evaluating the feasibility of using land treatment technology and assuring that the operational system can be adequately monitored.

For each hazardous waste evaluated during this project, a waste characterization program was conducted. Representative composite waste samples were obtained. Each waste was characterized for general physical and chemical parameters and for individual organic and inorganic constituents of concern. Table 21 contains a list of general waste characterization parameters that were determined for each waste. Specific organic and inorganic constituents of concern for each waste were selected as monitoring parameters in consultation with the U.S. EPA project officer.

TABLE 21. WASTE CHARACTERIZATION PARAMETERS

Density	Total organic carbon
Water content	Volatile organic constituents
Solids content (Residue)	Extractable organics
Ash content (Residue)	Metals
pH	Oil and grease

Waste characterization procedures were based on procedures given in Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods. Second Edition (U.S. EPA 1982). However, since the wastes chosen were complex mixtures that exhibited unique properties, compositions, and problems with respect to waste characterization, modification of some standard procedures and the use of additional referenced procedures were sometimes necessary. All standard procedures, modifications of standard procedures, and additional and alternative procedures used during this project are documented in this report.

Materials and Methods

Selection of Wastes--

Four listed hazardous wastes were selected for study in consultation with the U.S. EPA project officer. The wastes chosen are produced in high volume in the U.S., contain numerous organic and inorganic constituents, and represent a broad spectrum of physical, chemical, and toxicological characteristics. The specific wastes selected for study are listed below in Table 22.

TABLE 22. HAZARDOUS WASTES SELECTED FOR EVALUATION

Waste	EPA Hazardous Waste No.
Petroleum Refinery Wastes	
API Separator Sludge	K051
Slop Oil Emulsion Solids	K049
Wood Preserving Wastes	
Creosote	K001
Pentachlorophenol	K001

Petroleum Wastes--

API separator sludge--(K051) This waste is generated from the primary settling of wastewaters that enter the oily water sewer. API separator sludge typically consists of approximately 53 percent water, 23 percent oil, and 24 percent solids (Brown, K. W., and Associates 1980). The solids are largely sand and coarse silt, but also may contain significant quantities of heavy metals such as the metals that cause this waste to be listed as hazardous (i.e., chromium and lead). The heavy oils that settle in an API separator and become part of the bottom sludge will largely be composed of heavy tars, large multiple branched aliphatic compounds (paraffins), polyaromatic hydrocarbons, and coke fines. The proportions of the oily material in API separator sludge which are tar-like, paraffinic or polyaromatic are largely dependent on the source crude being refined. The amount of coke fines in the sludge should increase as the amount of thermal cracking used by the refinery increases.

Slop oil emulsion solids--(K049) This waste is generated from skimming the API separator. Slop oil emulsion solids are typically 40 percent water, 43 percent oil, and 12 percent solids. Chromium and lead are present in significant concentrations in the solid phase and are the reason this waste is listed as hazardous (Brown, K. W. and Associates 1980).

Wood Preserving Wastes--

Creosote--(K001) Creosote is a distillate from coal tar made by high temperature carbonization of bituminous coal. Creosote alone or in combination with coal tar or petroleum is a major preservative used in wood treatment (Merrill and Wade 1985). The principal classes of organic constituents present in creosote wastes are polyaromatic hydrocarbons and phenolics.

Pentachlorophenol (PCP)--(K001) Pentachlorophenol is widely used as a wood preservative. PCP has also been used for slime and algae control. The combined PCP-creosote sludge used in this experimental investigation contained polyaromatic hydrocarbons, phenolics, and PCP.

Physical Characterization of Wastes--

Density--

The density of a liquid waste can be determined by weighing a known volume of the waste in water or other liquid. A water insoluble viscous or solid waste is weighed in a calibrated flask containing a known volume and mass of water. The water displaced is equivalent to the volume of waste material added. A similar technique is used for the analysis of water soluble wastes by replacing water with a nonsolubilizing liquid for the volumetric displacement measurement. In this case a correction must be made for the density of the solvent used.

Water Content--

The water content of each waste was determined using ASTM Method D95-70 (Standard Method of Test for Water in Petroleum Products and Bituminous Materials by Distillation). A summary of the method is presented below.

The waste is heated under reflux with a water immiscible solvent which co-distills with the water in the sample. Condensed solvent and water are continuously separated on a trap. The water settles in the graduated section of the trap and the solvent is returned to the still.

Residue--

The term "residue" refers to solid matter that is suspended or dissolved in water or waste. Total residue is the term applied to the material that remains after evaporation of a sample and its subsequent drying in an oven at a defined temperature (103°C). Total includes "nonfilterable or suspended" and the "dissolved or filterable" residue.

The total volatile suspended residue is obtained by igniting the total suspended residue at 550°C. The test is used to obtain an approximation of the amount of organic matter present in the solid fraction of the waste.

Chemical Characterization of Wastes--

Inorganic Constituents--

Metals--A digest for the analysis of the total metal content of slop oil and API separator sludge samples was prepared using EPA Method 3030 for the acid digestion of oils, greases, and waxes (U.S. EPA 1982). Samples were prepared in triplicate. Standard quality control procedures were followed, including analysis of digested EPA reference material and reagent blanks. All analyses were performed using a Perkin-Elmer Model 6000 Inductively Coupled Plasma (ICP). Detection limits for As, Hg, Se, Cd, Pb, Ni, and V on the ICP were not satisfactory to define environmentally significant levels. Therefore, graphite furnace atomic absorption spectrophotometry (AA) was used for the analysis of Cd, Pb, Ni, and V. The As, Se, and Hg were analyzed by atomic adsorption (AA) using hydride generation.

The pentachlorophenol and creosote samples were digested using EPA Method 3050 (U.S. EPA 1982) for the acid digestion of sludges. Quality control procedures and specific methods for metal analysis were performed as described above. In addition, triplicate PCP and creosote samples were spiked with one of two EPA reference materials before digestion to determine percent recovery.

Organic Constituents--

Total organic carbon--The total organic carbon (TOC) content of the API separator sludge and creosote waste was determined. One gram of waste (dry weight) was thoroughly mixed with sand in a SPEX Ball Mill. An aliquot (0.01 to 1 g) of this waste/sand mixture was accurately weighed out and placed into a glass ampule along with 10 percent hydrochloric acid (1 ml/gram of mixture) and 200 mg of combusted copper oxide. The ampule was sealed and baked for 5 hrs at 550°C. After cooling, the contents of the ampule were analyzed using an Oceanography International (Model 524B) Carbon Analyzer.

Oil and grease--Oil and grease are defined as any material recovered as a substance soluble in fluorocarbon 113. The oil and grease content of each waste was determined using Method 413.1 (U.S. EPA 1979). In this procedure, the oils and greases are extracted by direct contact with an organic solvent, fluorocarbon 113. The solvent is separated from the aqueous and/or solid phases, dried and evaporated to determine the extractable residue by gravimetric techniques.

Volatile organic constituents--The volatile fraction of each waste was prepared using the purge and trap (Method 5030, U.S. EPA 1982). A portion of solid or liquid waste was dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol solution was combined with water in a specially designed purging chamber. Nitrogen was bubbled through the solution at ambient temperature, and the volatile components were transferred from the aqueous phase to the vapor phase. The vapor was swept through a Tenax^{R} sorbent column where the volatile components were trapped. After purging was completed, the sorbent column was heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column was heated to elute the volatile constituents, which were detected by flame ionization detector (FID) or gas chromatography/mass spectrometry (GC/MS).

Extractable organic constituents--The sample preparation and analysis scheme for extractable organics is shown in Figure 3. A 10-g aliquot of the waste in a 225-ml centrifuge bottle was diluted with 60 ml distilled, deionized water. The sample was homogenized with a Tekmar Tissumizer^R blending probe for 30 seconds to enhance the wetting of the sediment. Each sample was adjusted to pH 11 with 6 N sodium hydroxide. Three sequential extractions with 80-ml aliquots of dichloromethane were performed to isolate the base/neutral compounds and the pesticides. Following each addition of dichloromethane, the sample was homogenized for 30 seconds with a Tekmar Tissumizer^R blending probe, and centrifuged for 30 minutes at 2,500 revolutions per minute to promote phase separation. The three base/neutral extracts were combined and dried by passage through a short column of anhydrous sodium sulfate prior to concentration to 5 ml in a Kuderna-Danish evaporator. The waste samples were adjusted to pH 1 with 6 N hydrochloric acid, and the extraction, extract drying, and concentration steps were repeated to isolate the acidic compounds.

GC/MS analysis--The waste extracts were analyzed according to U.S. EPA standard methodology (U.S. EPA 1982) on a Hewlett-Packard (HP) 5985B Gas Chromatograph/ Mass Spectrometer/Data System (GC/MS/DS). The mass spectrometer was tuned prior to the analyses using perfluorotributylamine (PFTBA) and the Hewlett-Packard "Autotune" program, which optimizes ion source, mass filter, and electron multiplier parameters for optimum sensitivity, peak resolution and mass axis calibration. An abundance normalization program was also run to meet U.S. EPA specifications for spectral reproducibility.

The dichloromethane/waste sample extracts were analyzed using a 30 m x 0.32 mm I.D. SPB-5 bonded phase fused silica capillary column. Helium carrier gas was set at a split vent flow of 140 mL/min with column flow set at 1.4 mL/min (split ratio 1:100). A summary of the GC/MS analysis conditions used is presented in Table 23.

HPLC analysis--Polynuclear aromatic hydrocarbon compounds (PAHs) were determined using high performance liquid chromatography (HPLC) following Method 8310, (U.S. EPA 1982). A Perkin-Elmer HPLC system equipped with a quadruple solvent delivery system (Series 4), a UV detector (Model LC-85B), integrator (Model LCI-100) and reverse phase column (HC-ODS SIL-X), was used for analysis.

Chromatography conditions were as follows: isocratic for 1 minute with acetonitrile/water (40/60), linear gradient elution to 100 percent acetonitrile over 7 minutes, followed by a 3-minute hold at 100 percent acetonitrile.

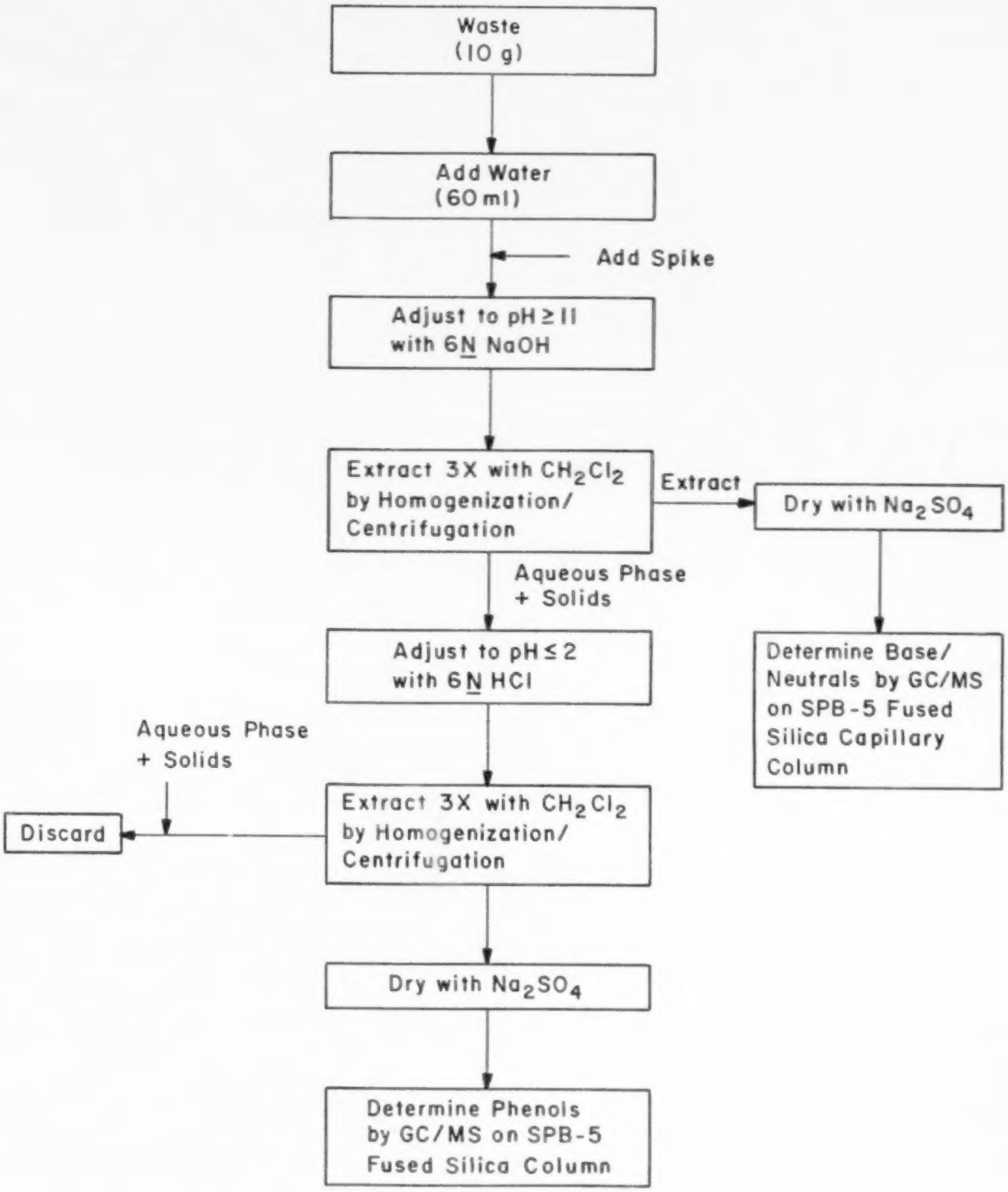
Waste
(10 g)
Add Water
(60 ml)
Add Spike
Adjust to pH ≥ 11
with 6N NaOH
Extract 3X with CH_2Cl_2
by Homogenization/
Centrifugation
Extract
Dry with Na_2SO_4
Aqueous Phase
+ Solids
Determine Base/
Neutrals by GC/MS
on SPB-5 Fused
Silica Capillary
Column
Adjust to pH ≤ 2
with 6N HCl
Aqueous Phase
+ Solids
Discard
Extract 3X with CH_2Cl_2
by Homogenization/
Centrifugation
Dry with Na_2SO_4
Determine Phenols
by GC/MS on SPB-5
Fused Silica Column

Figure 3. Scheme for the analysis of waste samples for organic constituents.

TABLE 23. GC/MS ANALYSIS CONDITIONS

Instrument:	
Gas chromatograph:	HP 5840
Mass spectrometer:	HP 5985B
Data system:	HP
Column:	30 m x 0.32 mm ID SPB-5 bonded phase fused silica capillary column (Supelco) routed directly into the ion source
Temperature program:	60°C (2 min) to 300°C at 4°C/min (base/neutrals/pesticides) 60°C (2 min) to 300°C at 8°C/min (acids)
Injector temperature:	290°C
Transfer line temperature:	300°C
Carrier gas:	Helium at 29 cm/sec
Splitless injection:	30 sec
Injection volume:	4 µl
Solvent:	Dichloromethane (samples) Methanol/dichloromethane (standards)
Mass spectrometer operating conditions:	
Ion source temperature:	280°C
Ionization energy:	70 eV
Trap current:	200 µA
Electron multiplier:	-1.75 kV
Scan range:	50-450 amu
Scan speed:	1-2 sec/scan

Biological Characterization of Waste--

A comprehensive assessment of the hazardous characteristics of a particular waste involves both chemical and biological analyses. Biological analysis provides information on potential interactions between waste and soil components that may not be shown by chemical identification of waste components. Biological analysis may also indicate the toxic and/or mutagenic potentials of the waste and waste-soil mixtures. In this study, acute toxicity of aqueous extracts of the waste samples was determined using the Microtox^{TM} system (Microbics Corp., Carlsbad, CA). The Ames *Salmonella typhimurium* mammalian microsome mutagenicity assay was used to assess the mutagenic potential of each hazardous waste.

Microtox Assay--

This procedure is described under "Waste Loading Rate Evaluation."

Ames Assay--

The procedures used for the Ames *Salmonella typhimurium* mammalian microsome mutagenicity assay for determining mutagenic potential of parent PAH compounds and soil metabolites are based on the methods described by Maron and Ames (1983). A schematic of the Ames assay is shown in Figure 4.

Sample preparation--The waste samples were extracted according to the extractable organics procedure described previously. The base/neutral fractions of all samples were tested for mutagenicity. In addition, the acid fraction of the pentachlorophenol waste was analyzed using the Ames assay. An aliquot of the concentrated extract of each sample was brought to dryness in a preweighed vial using a fine stream of purified air. The residue was brought up to a predetermined volume in dimethyl sulfoxide (DMSO) and sonicated for several minutes to ensure thorough mixing. A set of five dilutions ranging to 10^{-2} was prepared for initial mutagenicity screening. If necessary, additional dilutions were made for subsequent testing.

Experimental apparatus--The *Salmonella typhimurium* tester strain used for testing was TA-98, which detects frameshift mutagens. Genetic alterations to this strain and others included in the tester set have made them unable to grow in the absence of histidine. When the strains are placed on a histidine-free medium, the only colonies formed arise from cells that have reverted to histidine-independence. Spontaneous reversion rates are relatively constant for each bacterial strain, but addition of a chemical mutagen greatly increases the mutation value. Some mutagens require activation by mammalian microsomes. This activation is provided by addition of the S9 fraction derived from Aroclor 1254-induced rats. S9 can be prepared in the laboratory according to methods of Maron and Ames (1983) or may be purchased from commercial sources.

Procedures for preparation of the S9 microsomal mix and media are presented in Maron and Ames (1983).

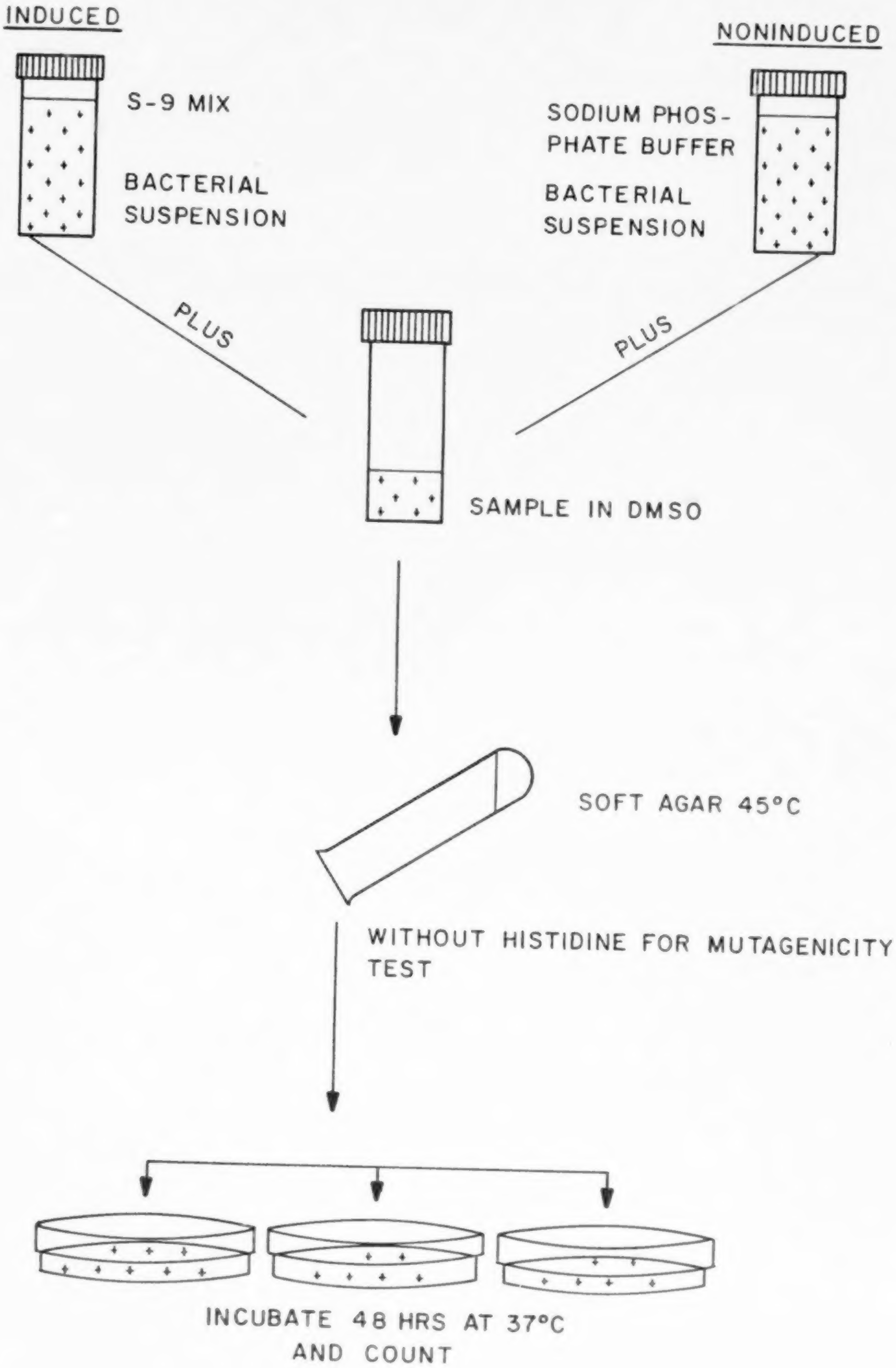
INDUCED
S-9 MIX
BACTERIAL SUSPENSION
NONINDUCED
SODIUM PHOS-PHATE BUFFER
BACTERIAL SUSPENSION
PLUS
PLUS
SAMPLE IN DMSO
SOFT AGAR 45°C
WITHOUT HISTIDINE FOR MUTAGENICITY TEST
INCUBATE 48 HRS AT 37°C AND COUNT

Figure 4. Schematic of the Ames assay.

The controls used in the Ames assay included plates with no chemical addition, solvent controls with DMSO added, and positive controls with known mutagens added. The known mutagens used included daunomycin-HCl without S9 and 2-aminofluorene with S9. Plates of each control type were prepared with and without S9. The bacterial suspension was added in each case.

Experimental procedure--For each Ames assay the following parameters were evaluated: 1) mutagenicity of the sample, 2) response of the strains to positive controls, 3) toxicity of the sample to the tester strains, and 4) sterility of samples and reagents.

Mutagenicity of the sample and of positive controls was determined using the plate incorporation method (Ames et al. 1975). A preliminary test and confirmatory test were performed for each sample based on recommendations of Williams and Preston (1983). For each test, five doses of the sample were evaluated both with and without S9, one dose per plate, with duplicate plates for each dose. For each plate, a mixture of 2.0 ml soft agar containing a trace of histidine, 0.1 ml bacterial suspension, 0.1 ml test material, and 0.5 ml of the S9 mix (if required) was overlaid on minimal media. The agar was allowed to harden and the plates were incubated 48 hours at 37°C.

Each confirmatory test involved repeating the assay using additional doses for providing the most active mutagenic response.

Known mutagens were included in each test to ensure that the strains were active and that the S9 preparation was activating promutagens to proximate mutagens.

Toxicity of the samples was determined by checking for the presence of background growth (lawn) on sample plates. This lawn results from the trace amount of histidine in the overlay (top) agar, and is necessary in most cases for mutagenesis to occur. A lawn which is sparse or absent compared to control plates with no chemical addition indicates toxicity to the tester strains, and visible colonies that appear are not necessarily revertants.

The sterility of all components of the assay--samples, positive controls, solvent, S9 mix and agar plates--was checked by plating without addition of the bacterial suspension.

Quality control procedures are especially important for the Ames assay to ensure that each component of the assay, prepared at different times and stored until use, is functioning properly at the time the assay is conducted. Quality control tests are performed periodically with respect to *Salmonella* strain validation and proper metabolic activation of S9. Strain validation ensures that the strains have retained the mutations for proper functioning. Proper metabolic activation ensures that any promutagen in the test material will be activated to the proximate mutagen successfully.

Data calculations--Raw data were obtained as revertants/plate and were scored on an automatic colony counter (New Brunswick Scientific Co., Inc.). Mean counts were calculated for replicate plates at each dose level and for positive and negative controls. Toxicity of samples was recorded when present, and results of sterility tests were noted. Mutagenic ratios were calculated for all sample concentration results. Mutagenic ratio is defined as:

$$\text{Mutagenic Ratio} = \frac{\text{number of colonies with sample}}{\text{number of colonies without sample}}$$

A test compound or sample is considered negative (nonmutagenic) if the mutagenic ratio is less than 2.5.

Recommendations on data production, handling, and analysis by de Serres and Shelby (1979) were followed in this research project. The recommendations concerning data presentation, definition of positive and negative results, and comments on statistical analysis represent a modification of the original protocol of Ames et al. (1975).

Results and Discussion

Physical Characterization of Wastes--

The water content density, specific gravity, and flash points of the four wastes are presented in Table 24. Results from the residue analysis are shown in Table 25.

Chemical Characterization of Wastes--

Inorganic Constituent--

Metals--Tables 26 and 27 present the results of metal analyses for the petroleum refinery and wood preserving wastes, respectively. Quality control results, including spiked samples for the metals analyses, are presented in Tables 28 - 31.

Organic Constituents--

Total organic carbon and oil and grease--The total organic carbon (TOC) and oil and grease content for three replicate samples are presented in Tables 32 and 33.

GC/MS analysis--The results of the GC/MS analyses of the base/ neutral fractions of waste extract are presented in Tables 34 and 35 for petroleum refinery wastes and in Tables 36 and 37 for wood preserving wastes. Table 38 lists compounds identified in the acid fraction of creosote and pentachlorophenol waste. No acid compounds were identified in the petroleum wastes. The compounds tentatively identified in each fraction are presented in their order of elution from the SPB-5 fused silica capillary column.

Compounds were identified by a comparison of sample mass spectra with mass spectra in the EPA/NIH mass spectral data base, which contains approximately 25,000 mass spectra (Heller and Milna 1978), or by manual interpretation. Identifications were considered tentative because the scope

TABLE 24. PHYSICAL CHARACTERIZATION OF WASTES

Waste	Water Content* (%)	Density (g/ml)	Specific Gravity	Flashpoint	pH
API Separator Sludge	47 ± 2.8+	0.986 ± 0.006	0.990 ± 0.008	92°F	4.9
Slop Oil	0.1 ± 0	0.806 ± 0.004	0.814 ± 0.005	<60°F	3.9
Creosote	33 ± 0.7	1.01 ± 0.08	1.01 ± 0.10	-	5.5
Pentachlorophenol	28 ± 0.7	0.824 ± 0.096	0.815 ± 0.098	-	5.4

*Method used: Standard Method of Test for Water in Petroleum Products and Bituminous Materials by Distillation. ASTM D95-70.

+Average of three replicates ± standard deviatios.

TABLE 25. CHARACTERIZATION OF RESIDUES IN HAZARDOUS WASTES

Waste Type	Total Residue (103°C) (mg/g)	Total Suspended Residue (103°C) (mg/g)	Total Volatile Suspended Residue (mg/g)
API Separator Sludge	257 ± 32*	77.0 ± 26.6	33.2 ± 10.0
Slop Oil	227 ± 27	1.77 ± 0.19	1.77 ± 0.19
Creosote	522 ± 9	384 ± 47	229 ± 36
Pentachlorophenol	422 ± 19	302 ± 14	189 ± 10

*Average of three replicates ± standard deviation.

TABLE 26. CHARACTERIZATION OF METALS IN PETROLEUM REFINERY WASTES*+

Metal	Concentration#	
	Separator Sludge	Slop Oil
	--- mg/Kg (corrected for blank ---	
Chromium	209 ± 8	1.8 ± 0.1
Zinc	260 ± 11	6 ± 2
Cadmium	0.41	0.02
Lead	11 ± 3	21 ± 2
Nickel	6 ± 2	2.1 ± 0.8
Vanadium	1.4	<0.05
Beryllium	<0.2	<0.2
Silver	3 ± 3	<1
Aluminum	279 ± 10	5 ± 4
Strontium	18 ± 1	0.3 ± 0
Barium	7.4 ± 0.6	2 ± 2
Copper	30 ± 2	0.7 ± 0.2
Arsenic	0.62 ± 0.02	<0.02
Selenium	<0.08	<0.02
Mercury	1.4 ± 0.7	<0.02
Antimony	<4	<4
Thallium	<5	<5
	--- g/kg (corrected for blank) ---	
Iron	1.32 ± 0.04	30

---

*Digestion Procedure: Method 3030, Acid Digestion of Oils, Greases or Waxes. Test Methods for Evaluating Solid Waste. SW-846, Second Edition (U.S. EPA 1982).

+Analytical Method: ICAP for all metals except arsenic; arsenic analyzed by AA-graphite furnace.

#Average of 3 replicate analysis ± standard deviations.

TABLE 27. CHARACTERIZATION OF METALS IN WOOD PRESERVING WASTES*+

Metal	Concentration#	
	Creosote	PCP
	--- mg/kg (corrected for blank) ---	
Osmium	<2.5	<2.5
Thallium	<12.5	<12.5
Arsenic	1.88 ± 0.17	1.31 ± 0.02
Mercury	<12.5	<12.5
Selenium	<12.5	<12.5
Molybdenum	< 1.25 ± 0.46	<1.25
Chromium	4.36 ± 0.46	3.02 ± 0.17
Antimony	<10 <10	
Zinc	62.7 ± 5.0	110 ± 2.12
Vanadium	3.26 ±0.29	1.72 ± 0.09
Cadmium	<0.5	<0.5
Lead	8.40 ± 0.89	13.0 ± 0.15
Nickel	3.70 ± 0.67	3.76 ± 0.57
Manganese	57.6 ± 4.4	107 ± 7
Beryllium	<0.1	<0.1
Silver	<1.2	<1.2
Strontium	9.92 ± 0.79	11.1 ± 0.2
Barium	252 ± 27	23.5 ± 0.5
Copper	15.1 ± 1.3	7.89 ± 0.34
	--- g/kg (corrected for blank) ---	
Iron	2.92 ± 0.25	1.93 ± 0.08
Aluminum	2.62 ± 0.17	1.24 ± 0.06

---

*Digestion Procedure: Method 3050, Acid Digestion of Sludges. Test Methods for Evaluating Solid Waste. SW-846, Second Edition (U.S. EPA 1982).

+Analytical Method: ICAP for all metals except arsenic; arsenic analyzed by AA-graphite furnace.

#Average of 3 replicate analysis ± standard deviations.

TABLE 28. CHARACTERIZATION OF METALS IN PETROLEUM REFINERY WASTES: QUALITY CONTROL DATA

Metal	Digested Quality Control Sample		Relative Error (%)	Blanks (μg/l)	Spike Recovery (Spiked After Digestion) (%)
	Measured Value (μg/l)	Actual Value (μg/l)			
Chromium	1140	1250	9	<25	-
Zinc	2000	2000	0	62	-
Cadmium	280	350	20	0.04	59
Lead	2230	2000	11	5	86
Nickel	1391	1500	7	20.0	102
Vanadium	4090	4250	4	<2.6	68
Beryllium	4240	4500	6	<5	-
Silver	100	-	-	<25	-
Aluminum	3730	4000	7	<100	-
Strontium	<5	-	-	<5	-
Barium	100	-	-	7	-
Copper	1920	1750	10	-	-
Arsenic	990	1500	34	3.8	-
Selenium	120	250	52	9.0	-
Mercury	50	40	25	<0.5	-
Antimony	-	-	-	-	-
Thallium	-	-	-	-	-
Iron	4710	4500	5	150	-

TABLE 29. CHARACTERIZATION OF METALS IN CREOSOTE WASTES: QUALITY CONTROL DATA FOR SPIKED CREOSOTE WASTE SAMPLES - HIGH AND LOW LEVEL

	High Level*			Low Level+		
Metal	Measured Value Spiked Waste- (mg/kg)#	Theoretical Value (mg/kg)**	Recovery (%)	Measured Value Spiked Waste- (mg/kg)#	Theoretical Value (mg/kg)**	Recovery (%)
Osmium	<2.5	-	-	<2.5	-	-
Thallium	<12.5	-	-	<12.5	-	-
Arsenic	3.58	4.17	85.8	2.44	2.68	91.3
Mercury	<12.5	-	-	<12.5	-	-
Selenium	<12.5	-	-	<12.5	-	-
Molybdenum	<1.25	-	-	<1.25	-	-
Chromium	7.58	7.97	95.0	4.51	4.52	99.8
Antimony	<10	-	-	<10	-	-
Zinc	61.5	67.5	91.7	63.9	60.3	100
Vanadium	14.2	14.4	97.8	5.23	59.3	88.2
Cadmium	0.67	0.52	119	<0.5	0.1	-
Lead	11.8	13.8	86.5	<7.5	8.89	-
Nickel	6.74	7.28	91.4	4.20	4.71	89.15
Manganese	56.9	62.1	92.2	58.7	55.05	107
Beryllium	10.2	11.0	92.1	0.74	0.82	90.25
Silver	<1.2	-	-	<1.2	-	-
Strontium++	9.37	10.1	93.2	9.74	9.37	102
Barium++	243	256.5	95.5	109.9	237.5	46.15
Copper	16.2	17.5	92.9	15.3	14.7	104.0
	(g/kg)	(g/kg)	(%)	(g/kg)	(g/kg)	(%)
Iron	2.86	2.98	96.8	2.85	2.76	103.3
Aluminum	2.49	2.49	100	2.55	2.49	102.5

---

*High level: Approximately 2 g pentachlorophenol waste spiked with 1 ml of EPA Control Sample No. WP475 #5. Spiked sample subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

+Low level: Approximately 2 g creosote waste spiked with 1 ml of EPA Quality Control Sample No. WP475 #4. Spiked sample subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

#Average of two replicate analysis. All concentrations are corrected for digested blank values.

**Theoretical value calculated as sume of average measured concentration corrected for sample size and amount added in QC sample.

++Note included in spike.

TABLE 30. CHARACTERIZATION OF METALS IN PENTACHLOROPHENOL WASTES: QUALITY CONTROL DATA FOR SPIKED PENTACHLOROPHENOL WASTE SAMPLES - HIGH AND LOW LEVEL

	High Level*			Low Level+		
Metal	Measured Value: Spiked Waste- (mg/kg)#	Theoretical Value (mg/kg)**	Recovery (%)	Measured Value Spiked Waste- (mg/kg)#	Theoretical Value (mg/kg)**	Recovery (%)
Osmium	<2.5	-	-	<2.5	-	-
Thallium	<12.5	-	-	<12.5	-	-
Arsenic	3.59	4.56	78.95	2.17	2.21	98.4
Mercury	<12.5	-	-	<12.5	-	-
Selenium	<12.5	-	-	<12.5	-	-
Molybdenum	<1.25	-	-	<1.25	-	-
Chromium	6.27	6.89	92.05	3.50	2.95	118.5
Antimony	<10	-	-	<10	-	-
Zinc	141.5	125	113.2	158.5	114.5	137
Vanadium	10.95	13.5	81.1	4.19	3.79	113.95
Cadmium	0.89	0.61	147	<0.5	0.1	-
Lead	16.95	19.25	88.1	15.2	15.6	97.5
Nickel	6.57	7.62	84.85	3.75	4.86	77.25
Manganese	104	114	91.25	94.7	102.3	92.8
Beryllium	10.45	11.65	89.7	0.77	0.86	90.05
Silver	<1.2	-	-	<1.2	-	-
Strontium++	10.55	11.65	90.55	11.15	10.7	105.15
Barium++	22.5	24.55	91.65	37.6	22.55	171.05
Copper	9.8	10.6	92.5	8.03	8.07	100.0
	(g/kg)	(g/kg)	(%)	(g/kg)	(g/kg)	(%)
Iron	1.92	2.03	94.6	1.15	1.20	96.5
Aluminum	1.21	1.33	91.30	1.15	1.20	96.5

---

*High level: Approximately 2 g pentachlorophenol waste spiked with 1 ml of EPA Control Sample No. WP475 #5. Spiked sample subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

+Low level: Approximately 2 g pentachlorophenol waste spiked with 1 ml of EPA Control Sample No. WP475 #4. Spiked sample subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

#All concentrations are corrected for digested blank values

**Theoretical value calculated as sum of average measured concentration corrected for sample size and amount added in QC sample.

++Not included in spike.

TABLE 31. CHARACTERIZATION OF METALS IN CREOSOTE AND PENTACHLOROPHENOL WASTES: QUALITY CONTROL DATA FOR EPA QUALITY CONTROL SAMPLES

Metal	Measured Value QC Sample #1* (μg/l)	Theoretical Value (μg/l)	Relative Deviation (%)	Measured Value QC Sample #2+ (μg/l)	Theoretical Value (μg/l)	Relative Deviation (%)	Blank (μg/l)
Osmium	<50	-	-	<50	-	-	<50
Thallium	<250	-	-	<250	-	-	<250
Arsenic	23.4	22	6.4	58.4	60	-2.7	<5
Mercury	<250	0.75	-	<250	3.5	-	<250
Selenium	<250	6	-	<250	30	-	<250
Molybdenum	<25	-	-	<25	-	-	<25
Chromium	<25	10	0	83	80	3.8	<25
Antimony	<200	-	-	<200	-	-	<200
Zinc	12	16	-25	77	80	3.8	12.7 (±4.7)
Vanadium	67	70	- 4.3	210	250	-16	<25
Cadmium	<10	2.5	-	11	13	-16	<10
Lead	<150	24	-	<150	120	-	<150
Nickel	<50	30	-	82	80	2.5	<50
Manganese	15	15	0.0	75	75	0.0	<2.5
Beryllium	20	20	0.0	245	250	-2.0	<2.5
Silver	<25	-	-	<25	-	-	<2.5
Strontium	<2.5	-	-	<2.5	-	-	<2.5
Barium#	22	-	-	19	-	-	<1.0
Copper	10	11	- 9.1	47	50	-6.0	<1.0
	(mg/l)	(mg/l)	(%)	(mg/l)	(mg/l)	(%)	(mg/l)
Iron	<0.02	0.02	-	<0.02	0.08	-100	<0.02
Aluminum	<0.1	0.06	-	0.5	0.45	11	<0.1

*QC Sample No. 1: 1 ml of EPA Quality Control Sample No. WP475 #4 subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

+QC Sample No. 2: 1 ml of EPA Quality Control Sample No. WP475 #5 subjected to digestion and analysis by ICAP (arsenic by AA-graphite furnace).

#No Ba reported in QC samples.

TABLE 32. TOTAL ORGANIC CARBON (TOC) CONTENT OF HAZARDOUS WASTE SAMPLES

Waste	TOC (mg/kg)*	Standard Deviation (mg/kg)	Coefficient of Variation (%)
API Separator Sludge	101,000	14,000	14
Creosote Waste	347,000	48,000	14

*Average of three replicates.

TABLE 33. CHARACTERIZATION OF OIL AND GREASE* IN HAZARDOUS WASTE SAMPLES

Waste Type	Oil and Grease (mg/kg)	Standard Deviation (mg/kg)	Coefficient of Variation (%)	Actual Value+ (mg/kg)
API Separator Sludge	3.5×10^5	2.5×10^4	7.2	N.A.
Slop Oil	4.6×10^5	4.9×10^4	11	N.A.
Creosote	3.7×10^5	1.2×10^4	3.1	N.A.
Pentachlorophenol	5.2×10^5	1.5×10^4	2.9	N.A.
QA/QC Samples:				
#2 Fuel Oil	9.4×10^5	1.0×10^4	1.1	$>8.8 \times 10^5$
EPA-API Reference Oil: Prudhoe Bay Crude Oil (WP 681)	8.6×10^5	1.0×10^4	1.6	$>8.8 \times 10^5$

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*Procedure: U.S. EPA procedure (Robert S. Kerr Environmental Research Laboratory Standard Operating Procedure (SOP)-21.

+N.A. = Not applicable.

TABLE 34. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN API SEPARATOR SLUDGE WASTE (BASE NEUTRAL FRACTION) BY GC/MS

Compound	Formula	Molecular Weight	Retention Time (minutes)
Heptane	C_6H_{16}	100.	0.8
Hexane, 2, 5-Dimethyl, Heptane, 2-Methyl	C_8H_{18}	114.	1.0
Cyclopentane, ethyl-methyl, or alkane	C_8H_{16}	112.	1.1
Benzene, methyl	C_7H_8	92.	2.1
Nonane	C_9H_{20}	128.	3.0
Benzene, dimethyl	C_8H_{10}	106.	4.4
Nonane, 4-methyl, actane, dimethyl	$C_{10}H_{22}$	142.	4.6
Benzene, dimethyl	C_8H_{10}	106.	5.4
Decane	$C_{10}H_{22}$	142.	6.1
Decane, 4-methyl	$C_{11}H_{24}$	156.	6.6
Benzene, propyl	C_9H_{12}	120.	7.2
Benzene, ethyl methyl; Benzene, trimethyl	C_9H_{12}	120.	7.5
Benzene, alkyl substituted	C_9H_{12}	120.	7.7
Benzene, trimethyl; Benzene, ethyl methyl	C_9H_{12}	120.	8.1
Benzene, trimethyl; Benzene, ethyl methyl	C_9H_{12}	120.	8.4
Undecane	$C_{11}H_{24}$	156.	9.1
Benzene, trimethyl; Benzene, ethyl methyl	C_9H_{12}	120.	9.4
Benzene, diethyl; Benzene, methyl propyl	$C_{10}H_{14}$	134.	9.8
Benzene, diethyl; Benzene, methyl propyl	$C_{10}H_{14}$	134.	10.0
Benzene, diethyl; Benzene, methyl propyl	$C_{10}H_{14}$	134.	10.2
Benzene, ethyl dimethyl; Benzene, tetramethyl; etc.	$C_{10}H_{14}$	134.	10.5
Benzene, ethyl dimethyl; Benzene, tetramethyl; etc.	$C_{10}H_{14}$	134.	10.8
Dodecane	$C_{12}H_{26}$	170.	11.4
Benzene, ethyl dimethyl; Benzene, tetramethyl, etc.	$C_{10}H_{14}$	134.	11.7
Tridecane	$C_{13}H_{28}$	184.	13.4

TABLE 34. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Naphthalene, Azulene	$C_{10}H_8$	128.	14.1
Tetradecane	$C_{14}H_{30}$	198.	15.2
Naphthalene, methyl	$C_{11}H_{10}$	142.	15.9
Naphthalene, methyl	$C_{11}H_{10}$	142.	16.5
Pentadecane	$C_{15}H_{32}$	212.	16.9
Tetradecane, trimethyl	$C_{17}H_{36}$	240.	17.5
1,1'-Biphenyl	$C_{12}H_{10}$	154.	17.7
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	17.9
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	18.3
Hexadecane	$C_{16}H_{34}$	226.	18.4
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	18.7
1,1'-Biphenyl, methyl	$C_{13}H_{12}$	168.	19.4
Heptadecande	$C_{17}H_{36}$	240.	20.0
Naphthalene, trimethyl	$C_{13}H_{14}$	170.	20.2
Naphthalene, trimethyl	$C_{13}H_{14}$	170.	20.6
Octadecane	$C_{18}H_{38}$	254.	21.4
Nonadecane	$C_{19}H_{40}$	268.	22.7
Eicosane	$C_{20}H_{42}$	282.	24.0
Phenanthrene, anthracene	$C_{14}H_{10}$	178.	24.6
Heneicosane	$C_{21}H_{44}$	296.	25.2
Dibenzothiophene, methyl; 9H-thioxanthene	$C_{13}H_{10}S$	198.	25.4
Dibenzothiophene, methyl; 9H-thioxanthene	$C_{13}H_{10}S$	198.	25.7
Anthracene/Phenanthrene methyl substituted	$C_{15}H_{12}$	192.	26.0
Docosane	$C_{22}H_{46}$	310.	26.2
Anthracene/phenanthrene methyl substituted	$C_{15}H_{12}$	192.	26.4
Dibenzothiophene, dimethyl	$C_{14}H_{12}S$	212.	26.9
Tricosane	$C_{23}H_{48}$	324.	27.4
Phenanthrene/anthracene, dimethyl	$C_{16}H_{14}$	206.	27.6
Phenanthrene/anthracene, dimethyl	$C_{16}H_{14}$	206.	27.9
Tetracosane	$C_{24}H_{50}$	338.	28.5
Phenanthrene/anthracene, Trimethyl	$C_{17}H_{16}$	220.	28.9
Phenanthrene/anthracene, Trimethyl	$C_{17}H_{16}$	220.	29.2
Pentacosane	$C_{25}H_{52}$	352.	29.5

TABLE 34. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Hexacosane	$C_{26}H_{54}$	366.	30.6
Heptacosane	$C_{27}H_{56}$	380.	31.5
Octacosane	$C_{28}H_{58}$	394.	32.5
Nonacosane	$C_{29}H_{60}$	408.	33.7
	$C_{30}H_{62}$	422.	35.

TABLE 35. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN SLOP OIL EMULSION WASTE (BASE/NEUTRAL FRACTION) BY GC/MS

Compound	Formula	Molecular Weight	Retention Time (minutes)
Dichloromethane	CH_2Cl_2	85.	
Hexane, 2,2-dimethyl; or Butane, 2,2,3,3 tetramethyl	C_8H_{18}	114.	0.8
Heptane	C_6H_{16}	100.	1.0
Methyl benzene	C_7H_8	92.	2.3
Nonane	C_9H_{20}	128.	3.5
Benzene, dimethyl	C_8H_{10}	106.	5.1
Benzene, dimethyl	C_8H_{10}	106.	5.9
Decane	$C_{10}H_{22}$	142.	6.8
Benzene, propyl	C_9H_{12}	120.	7.5
Benzene, ethyl methyl substituted	C_9H_{12}	120.	7.9
Cyclohexane, butyl, or thiophthene	$C_{10}H_{20}$, $C_6H_4S_2$	140., 140.	8.1
Benzene, ethyl methyl; or benzene, trimethyl	C_9H_{12}	120.	8.4
Benzene, trimethyl; or benzene, ethyl methyl	$C_9H^{1}{}_{2}$	120.	8.8
Benzene, methyl propyl; benzene, ethyl dimethyl, or benzene, tetramethyl	$C_{10}H_{14}$	134.	9.3
Undecane	$C_{11}H_{24}$	156.	9.5
Benzene, 1,2,3-trimethyl	C_9H_{12}	120.	9.7
Benzene, diethyl	$C_{10}H_{14}$	134.	10.1

TABLE 35. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Benzene, methylpropyl; or benzene, tetramethyl; or benzene, ethyldimethyl	$C_{10}H_{14}$	134.	10.3
Benzene, tetramethyl; benzene, ethyldimethyl; or benzene, methylpropyl	$C_{10}H_{14}$	134.	10.7
Benzene, ethyl-dimethyl substituted; benzene, 1-methyl-4-(1-methylethyl)-; or benzene, diethyl; acenaphthylene	$C_{10}H_{14}$,$C_{12}H_8$	134.,152	10.9
Alkyl-substituted benzene	$C_{11}H_{16}$	148.	11.1
Dodecane	$C_{12}H_{26}$	170.	11.7
Benzene, ethyl dimethyl substituted; or benzene, methyl-dipropyl	$C_{10}H_{14}$	134.	11.8
Benzene, diethylmethyl	$C_{11}H_{16}$	148.	12.1
Benzene, diethylmethyl; or benzene, ethyltrimethyl	$C_{11}H_{16}$	148.	12.5
Indane, dimethyl; naphthalene, or tetrahydromethyl; benzene, pentamethyl or alkyl substituted benzene	$C_{11}H_{14}$, $C_{11}H_{16}$	146., 148	13.3
Tridecane	$C_{13}H_{28}$	184.	14.2
Naphthalene	$C_{10}H_8$	128.	14.4
Tetradecane	$C_{14}H_{30}$	198.	15.4
Naphthalene, -methyl	$C_{11}H^{1}{}_{0}$	142.	16.2
Naphthalene, -methyl	$C_{11}H_{10}$	142.	16.6
Pentadecane	$C_{15}H_{32}$	212.	17.1

TABLE 35. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Naphthalene, dimethyl substituted	$C_{12}H_{12}$	156.	18.5
Hexadecane	$C_{16}H_{34}$	226.	18.7
Naphthalene, dimethyl substituted	$C_{12}H_{12}$	156.	18.8
Naphthalene, methyl ethyl	$C_{13}H_{14}$	170.	19.0
Naphthalene, trimethyl, or naphthalene, methyl ethyl	$C_{13}H_{14}$	170.	19.5
Naphthalene, alkyl substituted	$C_{13}H_{14}$	170.	
Naphthalene, alkyl substituted	$C_{13}H_{14}$	170.	20.1
Heptadecane	$C_{17}H_{36}$	240.	20.2
Naphthalene, trimethyl substituted	$C_{13}H_{14}$	170.	20.4
Naphthalene, trimethyl substituted	$C_{13}H_{14}$	170.	20.7
Naphthalene, tetramethyl; or naphthalene, alkyl substituted	$C_{14}H_{16}$	184.	20.9
Biphenyl, dimethyl; or biphenyl ethyl	$C_{14}H_{14}$	182.	
Octadecane	$C_{18}H_{38}$	254.	21.6
Naphthalene, methyl, isopropyl	$C_{14}H_{16}$	184.	22.2
Naphthalene, dimethyl, isopropyl; naphthalene, alkyl substituted	$C_{15}H_{18}$, $C_{14}H_{16}$	198., 184.	22.5
Nonadecane	$C_{19}H_{40}$	268.	23.0

TABLE 35. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Eicosane	$C_{20}H_{42}$	282.	24.2
Phenanthrene/anthracene	$C_{14}H_{10}$	178.	24.7
Heneicosane	$C_{21}H_{44}$	296.	25.3
Anthracene; phenanthrene, methyl substituted	$C_{15}H_{12}$	192.	26.1
Anthracene; phenanthrene, methyl substituted	$C_{15}H_{12}$	192.	26.2
Docosane	$C_{22}H_{46}$	310.	26.4
Anthracene; phenanthrene, methyl substituted	$C_{15}H_{12}$	192.	26.6
Dibenzothiophene, dimethyl	$C_{14}H_{12}S$	212.	26.9
Dibenzothiophene, dimethyl	$C_{14}H_{12}S$	212.	27.1
Phenanthracene, anthracene, dimethyl substituted	$C_{16}H_{14}$	206.	27.4
Penanthrene, dimethyl substituted; anthrazene	$C_{16}H_{14}$	206.	27.8
Benzo[ghi]fluoranthene	$C_{18}H_{10}$	226.	28.0
Tetracosane	$C_{24}H_{50}$	338.	28.4
Phenanthrene, trimethyl; anthrene, trimethyl	$C_{17}H_{16}$	220.	28.9
Fluoranthene; pyrene	$C_{16}H_{10}$	202.	29.2
Pentacosane	$C_{25}H_{52}$	352.	29.5
Hexacosane	$C_{26}H_{54}$	366.	30.5
Heptacosane	$C_{27}H_{56}$	380.	31.5
Octacosane	$C_{28}H_{58}$	394.	32.5
Nonacosane	$C_{29}H_{60}$	408.	33.6

TABLE 36. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN CREOSOTE WASTE (BASE/NEUTRAL FRACTION) BY GC/MS

Compound	Formula	Molecular Weight	Retention Time (minutes)
Cyclohexane	C_6H_{12}	84.	5.5
Trichloroethane	C_2HCl_3	130.	6.4
Benzene, Ethyl, Me	C_9H_{10}	118.	13.8
Benzene, Ethynyl, Me	C_9H_8	116.	14.0
Naphthalene, Methyl	$C_{11}H_{10}$	142.	18.3
1,1'-Biphenyl or Acenaphthylene-1,2-Dihydro	$C_{12}H_{10}$	154.	19.5
Naphthalene, Ethyl or Dimethyl	$C_{12}H_{12}$	156.	
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	19.9
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	20.2
Naphthalene, Dimethyl	$C_{12}H_{12}$	156.	20.4
1,1'-Biphenyl, Methyl or Benzene, 1,1'-Methylenebis	$C_{13}H_{12}$	168.	20.9
Biphenylene or acenaphthylene		153. or 154	21.2
Dibenzofuran	$C_{12}H_8O$	168.	21.5
9H-Fluorene	$C_{13}H_{10}$	166.	22.4
1,1'-Biphenyl, Methyl, or Naphthalene, 1-(2-propanyl)	$C_{13}H_{12}$	168.	22.8
Phenanthrene, 9,10-Dihydro	$C_{14}H_{12}$	180.	23.6
9H-Fluorene, Methyl	$C_{14}H_{12}$	180.	23.9
Octadecane	$C_{18}H_{38}$	254.	24.3
Phenanthrene or Anthracene	$C_{14}H_{10}$	178.	24.9
Anthracene or Phenanthrene	$C_{14}H_{10}$	178.	25.1
9H-Carbazole	$C_{12}H_9N$	167.	25.5
Phenanthrene, Methyl or Anthracene, Methyl	$C_{15}H_{12}$	192.	26.2
Phenanthrene, Methyl or Anthracene, Methyl	$C_{15}H_{12}$	192.	26.3
Naphthalene, Phenyl	$C_{16}H_{12}$	204.	26.9
Pyrene, or Fluoranthene	$C_{16}H_{10}$	202.	28.0
Pyrene, or Fluoranthene	$C_{16}H_{10}$	202.	28.6
11H-Benzo(a)fluorene or Pyrene, Methyl	$C_{17}H_{12}$	216.	29.2
11H-Benzo(a)fluorene or Pyrene, Methyl	$C_{17}H_{12}$	216.	29.5
11H-Benzo(a)fluorene or Pyrene, Methyl	$C_{17}H_{12}$	216.	29.6
Benz(a)anthrancene, or Triphenylene, or Chrysene	$C_{18}H_{12}$	228.	32.1
Benz(a)anthracene, or Triphenylene, or Chrysene	$C_{18}H_{12}$	228.	32.2

TABLE 37. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN PENTACHLOROPHENOL WASTE (BASE/NEUTRAL FRACTION) BY GC/MS

Compound	Formula	Molecular Weight	Retention Time (minutes)
Benzene, methyl	C_7H_8	92.	8.4
Pyridine, methyl	C_6H_7N	93.	9.5
Benzene, ethyl	C_8H_{10}	106.	10.6
Benzene, dimethyl	C_8H_{10}	106.	10.7
Pyridine, dimethyl	C_7H_9	107.	11.0
Benzene, ethenyl	C_8H_8	104.	11.2
Pyridine, dimethyl	C_7H_9N	107.	11.9
Pyridine, dimethyl	C_7H_9N	107.	12.3
Benzene, propyl	C_9H_{12}	120.	12.5
Benzene, isopropyl	C_9H_{12}	120.	12.6
Benzene, trimethyl	C_9H_{12}	120.	12.8
Benzene, ethyl-methyl;	C_9H_{12}	120.	13.0
and Benzene, ethenyl-methyl	C_9H_{10}	118.	
Benzonitrile;	C_7H_5N	103.	13.1
Pyridine, trimethyl; and	$C_8H_{11}N$	121.	
Benzene, trimethyl	C_9H_{12}	120.	
Benzene, trimethyl	C_9H_{12}	120.	13.8
Benzene, ethenyl-methyl	C_9H_8	116.	14.4
Benzene, ethyl-dimethyl	$C_{10}H_{14}$	134.	14.4
Undecane	$C_{11}H_{24}$	156.	15.0
Benzofuran, methyl	C_9H_8O	132.	15.3
Benzene, tetramethyl	$C_{10}H_{14}$	134.	15.6
1 H-Indene, 2,3-dihydro or Benzene, methyl-propenyl	$C_{10}H_{12}$	132.	16.0
1 H-Indene, methyl	$C_{10}H_{10}$	130.	16.3
Dodecane	$C_{12}H_{26}$	170.	16.6
Naphthalene (or Azulene)	$C_{10}H_8$	128.	16.9
Quinoline or Isoquinoline	C_9H_7N	129.	17.7
Quinoline or Isoquinoline	C_9H_7N	129.	18.0
Tridecane	$C_{13}H_{28}$	184.	18.2
Naphthalene, methyl	$C_{11}H_{10}$	142.	18.6
Naphthalene, methyl	$C_{11}H_{10}$	142.	18.9
Quinoline, methyl	$C_{10}H_9N$	143.	19.5
Tetradecane	$C_{14}H_{30}$	198.	19.6
Biphenyl	$C_{12}H_{10}$	154.	19.8
Naphthalene, ethyl	$C_{12}H_{12}$	156.	20.0
Naphthalene, dimethyl	$C_{12}H_{12}$	156.	20.2
Naphthalene, dimethyl	$C_{12}H_{12}$	156.	20.4
Biphenyl, methyl	$C_{13}H_{12}$	168.	21.2
Acenaphthalene	$C_{12}H_{10}$	154.	21.4
Dibenzofuran	$C_{12}H_8O$	168.	21.8

TABLE 37. CONTINUED

Compound	Formula	Molecular Weight	Retention Time (minutes)
Naphthalene, trimethyl	$C_{13}H_{14}$	170.	22.1
Hexadecane	$C_{16}H_{34}$	226.	22.2
9 H-Fluorene or 1 H-Phenalene	$C_{13}H_{10}$	166.	22.7
Fluorene, methyl and	$C_{14}H_{12}$	180.	23.0
Biphenyl, methyl	$C_{13}H_{12}$	168.	23.0
Biphenyl, methyl	$C_{13}H_{12}$	168.	23.1
Xanthene; or Dibenzofuran, methyl	$C_{13}H_{10}O$	182.	23.4
Phenanthrene, dihydro	$C_{14}H_{12}$	180.	23.9
9 H - Fluorene, methyl	$C_{14}H_{12}$	180.	24.1
Phenanthrene	$C_{14}H_{10}$	178.	25.2
Anthracene	$C_{14}H_{10}$	178.	25.4
9 H-Carbazole	$C_{12}H_{9}N$	167.	25.8
Dibenzothiophene, methyl	$C_{13}H_{10}S$	198.	26.1
Dibenzothiophene, methyl	$C_{13}H_{10}S$	198.	26.2
Phenanthrene, methyl or Anthracene, methyl	$C_{15}H_{12}$	192.	26.6
Phenanthrene, methyl or Anthracene, methyl	$C_{15}H_{12}$	192.	26.7
4 H-Cyclopenta[def]phenanthrene	$C_{15}H_{10}$	190	26.8
Naphthalene, phenyl	$C_{16}H_{12}$	204.	27.2
Pentadecane; Tetradecane, methyl; or Tridecane, dimethyl	$C_{15}H_{32}$	212.	27.7
Phenanthrene, dimethyl	$C_{16}H_{14}$	206.	28.0
Pyrene or Fluoranthene	$C_{16}H_{10}$	202.	28.3
Pyrene or Fluoranthene	$C_{16}H_{10}$	202.	28.9
9-Anthracene carbonitrile	$C_{15}H_{9}N$	203.	29.3
Pyrene, methyl or benzofluorene	$C_{17}H_{12}$	216.	29.8
Pyrene, methyl or benzofluorene	$C_{17}H_{12}$	216.	29.9
Benzothionaphthalene	$C_{16}H_{10}S$	234.	31.6
Triphenylene, Benzanthracene or chrysene	$C_{18}H_{12}$	228.	31.7
Benzofluoranthene and	$C_{18}H_{10}$	226.	31.8
Benzophenanthrene, Benzanthracene, Triphenylene, or Chrysene	$C_{18}H_{12}$	228.	

TABLE 38. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN CREOSOTE WASTE AND PENTACHLOROPHENOL WASTE (ACID FRACTION) BY GC/MS

Compound	Formula	Molecular Weight	Retention Time (minutes)
THF	C_4H_8O	72	4.8
Phenol	C_6H_6O	94	12.5
Phenol, Methyl	C_7H_8O	108	13.9
Phenol, Methyl	C_7H_8O	108	14.3
Phenol, Dimethyl	$C_8H_{10}O$	122	15.0
Phenol, Dimethyl	$C_8H_{10}O$	122	15.6
Phenol, Dimethyl or Ethyl	$C_8H_{10}O$	122	15.9
Phenol, Dimethyl or Ethyl	$C_8H_{10}O$	122	16.3
Phenol, Ethyl-Methyl	$C_9H_{12}O$	136	17.0
Phenol, Ethyl-Methyl	$C_9H_{12}O$	136	17.3
Phenol, Pentachloro	C_6HCl_5O	264	24.6

of this research project did not include confirmatory analysis with authentic standards. Many of the mass spectra were also manually interpreted, especially when a match via library search was unsuccessful.

Volatile organics--Tables 39 and 40 present the GC/MS analysis of the volatile fraction of the separator sludge, slop oil, creosote, and pentachlorophenol wastes. The prominent peak in all samples analyzed was identified as naphthalene. Additionally, various substituted naphthalenes, substituted benzenes, and hexane were prominent in the PCP waste as were substituted naphthalenes in the creosote waste due to the high oil content of these samples. Phenol was also tentatively identified in the creosote waste.

HPLC analysis--In addition to GC/MS analysis, HPLC analysis was used for identification and quantification for individual PAH compounds. Concentrations of individual PAH compounds determined by HPLC for three replicate samples of each waste are presented in Table 41.

GC/MS Analysis of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) in Pentachlorophenol Waste--Two subsamples of the pentachlorophenol waste were analyzed by GC/MS for PCDDs and PCDFs by U.S. EPA Environmental Monitoring Systems Laboratory (EMSL), Las Vegas, Nevada, following Method 8280 (U.S. EPA 1982). Results are presented in Table 42.

Biological Characterization--

Microtox--

Each waste was characterized for toxicity of the water soluble fraction (WSF) using the Microtox assay. Results for each waste are presented in Table 43. Average values for EC50 indicate that wood preserving wastes exhibited greater WSF toxicity than petroleum wastes. However results indicated that all wastes exhibited a high degree of WSF toxicity as measured by the Microtox assay.

Ames--

The mutagenic potential of each waste was determined using the Ames *Salmonella* test. Results for the base/neutral fraction of creosote are presented in Figure 5. This fraction exhibited relatively low level mutagenicity with S9 activation, while no mutagenicity is indicated without addition of S9. Toxicity (as evidenced by a sparse background lawn) was indicated at the 400 g/plate dose with S9 and at the 240 g/plate dose without S9.

Two sample extracts of the pentachlorophenol waste were tested for mutagenicity. The results for the base/neutral fraction and the acid fraction of PCP are presented in Figures 6 and 7, respectively.

The base/neutral extract with added S9 exhibited low level mutagenicity which decreased at higher doses. There was an indication of toxicity to the Salmonella bacteria at the 641 g/plate dose with definite toxicity present at higher doses. When no S9 was added with the sample, no mutagenicity was

TABLE 39. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN API SEPARATOR SLUDGE AND SLOP OIL WASTE SAMPLES (VOLATILE FRACTION) BY GC/MS

Compound	Molecular Weight	Retention Time (min)
Cyclohexane	84	5.93
2,2,4-trimethylpentane	114	6.53
Methyl-cyclohexane	98	7.45
Toluene	92	8.55
1,3-dimethyl-trans-cyclohexane	112	8.82
Octane	114	9.28
Ethyl-cyclohexane	112	10.15
p-xylene	106	10.95
o-xylene	106	11.5
1-ethyl-3-methylbenzene	120	12.9
trimethylbenzene	120	13.57
1-methyl-4-propyl-benzene	134	14.6
1-methyl-2 or 4(1-methylethyl)benzene	134	14.8
1-methyl-3(1-methylethyl)benzene, or 1-ethyl-2,4-dimethylbenzene	134	15.17
(1,1-dimethylbutyl)benzene	162	15.3
Undecane	156	15.35
1-ethyl-3,5- or 2,4- or 1,2-dimethylbenzene	134	15.85
1-ethyl-3,5-dimethyl or 1,2,3/4,5-tetramethylbenzene	134	15.93
Octacosane	394	17.05
Naphthalene	128	17.2
1-ethyl-1-methyl-cyclopentane	112	17.83
2,3-dihydro-1,6-dimethyl-1H-indene	146	18.4
Octadecane	254	18.6
Methyl-naphthalene	142	18.98
2-methyl-naphthalene	142	19.27
Pentacosane	352	20.07
1,1'-biphenyl	154	20.2
Ethylnaphthalene	156	20.47
Dimethyl-naphthalene	156	20.62
Ethyl-naphthalene	156	21.4
2-(1-methylethyl)-naphthalene	170	22.02
Trimethyl-naphthalene	170	22.3
1,6,7-trimethylnaphthalene	170	22.83
1-methyl-9HFluorene	180	24.75
Phenanthrene	178	25.73
4-methylphenanthrene	192	27.02
Dimethyl-phenanthrene	206	28.48

TABLE 40. ORGANIC COMPOUNDS TENTATIVELY IDENTIFIED IN PCP AND CREOSOTE WASTE SAMPLES (VOLATILE FRACTION) BY GC/MS

Compound	Molecular Weight	Retention Time (min)
PCP Waste Data		
Hexane	86	1:50
2-methyl-4,6-octadiyn-3-one	134	11:32
Ethylbenzene	106	11:32
1-propynl-benzene	118	18:08
1-ethynyl-4-methylbenzene	116	19:16
Azulene	128	22:56
Naphthalene	128	22:56
Benzothiazole	135	25:34
2-methylnaphthalene	142	26:05
Dimethylnaphthalene	156	29:50
Creosote Waste Data		
2,4,4-trimethylhexane	128	20:20
Phenol	94	20:29
Benzothiazole	135	21:39
Naphthalene	128	23:02
1,2-benzisothiazole	135	24:24
Methylnaphthalene	142	25:37

TABLE 41. CONCENTRATION OF INDIVIDUAL PAH COMPOUNDS IN WASTES DETERMINED BY HPLC

Compound	Concentration in Waste (mg/kg)*			
	API Separator Sludge	Slop Oil	Creosote	Pentachlorophenol
Naphthalene	580 ± 87 (15%)	2,500 ± 700 (28%)	28,000 ± 1,200 (4%)	42,000 ± 28,000 (67%)
Acenaphthalene	480 ± 100 (21%)	<15	3,600 ± 1,000 (28%)	<2,000
Acenaphthene	<12	<10	180,000 ± 40,000 (22%)	<13,000
Fluorene	29 ± 33 (114%)	440 ± 300 (68%)	23,000 ± 5,900 (26%)	<22,000
Phenanthrene	810 ± 140 (17%)	3,600 ± 2,100 (58%)	76,000 ± 15,000 (20%)	52,000 ± 6,200 (12%)
Anthracene	110 ± 27 (25%)	480 ± 93 (19%)	15,000 ± 6,800 (45%)	11,000 ± 6,800 (62%)
Fluoranthene	5,500 ± 290 (5%)	18,000 ± 5,000 (28%)	72,000 ± 17,000 (24%)	46,000 ± 6,200 (13%)
Pyrene	6,000 ± 440 (7%)	23,000 ± 6,700 (29%)	64,000 ± 12,000 (19%)	56,000 ± 13,000 (23%)
Benzo(a)anthracene	1,400 ± 58 (4%)	2,000 ± 1,100 (55%)	7,400 ± 1,600 (22%)	16,000 ± 2,400 (15%)
Chrysene	570 ± 310 (54%)	1,100 ± 150 (14%)	8,300 ± 2,100 (25%)	6,900 ± 2,200 (32%)
Benzo(b)fluoranthene	<3	340 ± 140 (41%)	3,000 ± 700 (23%)	10,100 ± 5,100 (51%)
Benzo(k)fluoranthene	310 ± 62 (20%)	160 ± 42 (26%)	2,400 ± 460 (19%)	<300
Benzo(a)pyrene	170 ± 73 (43%)	260 ± 200 (77%)	2,700 ± 380 (14%)	<280
Benzo(ghi)pyrene	<10	59 ± 18 (31%)	1,100 ± 280 (25%)	<100
Dibenz(a,h)anthracene	40 ± 11 (28%)	15 ± 1 (7%)	<1,200	<250
Indeno(1,2,3-cd)pyrene	61 ± 25 (41%)	88 ± 19 (22%)	820 ± 76 (9%)	<60

*Average concentration of three replicate analyses ± one standard deviation (coefficient of variation %).

TABLE 42. CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN PENTACHLOROPHENOL WASTE BY GC/MS*

	Concentration (ppb)	
	Sample P2T-1	Sample P2T-2
Dibenzo-p-dioxins (DD)		
TetrachloroDD	none detected (<10 ppb)	none detected (<10 ppb)
PentachloroDD	none detected (<10 ppb)	none detected (<10 ppb)
HexachloroDD	1,714	1,532
HeptachloroDD	25,019	27,810
OctachloroDD	80,053	73,123
Dibenzofurans (DF)		
TetrachloroDF	16.3	8.2
PentachloroDF	77.4	6.1
HexachloroDF	1,760	1,643
HeptachloroDF	4,418	4,748
OctachloroDF	6,030	7,074

*Analysis of EMSL Laboratory U.S. EPA, Las Vegas, Nevada, Method 8280 (SW-846 EPA).

TABLE 43. TOXICITY OF WATER SOLUBLE FRACTION MEASURED BY THE MICROTOX ASSAY FOR HAZARDOUS WASTE SAMPLES

Waste	EC50(5,15°)* (vol %)+
Creosote	0.3
PCP	0.7
API Separator Sludge	6.0
Slop Oil Emulsion Solids	1.3

*EC50(5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

+Results given are means of two replicates.

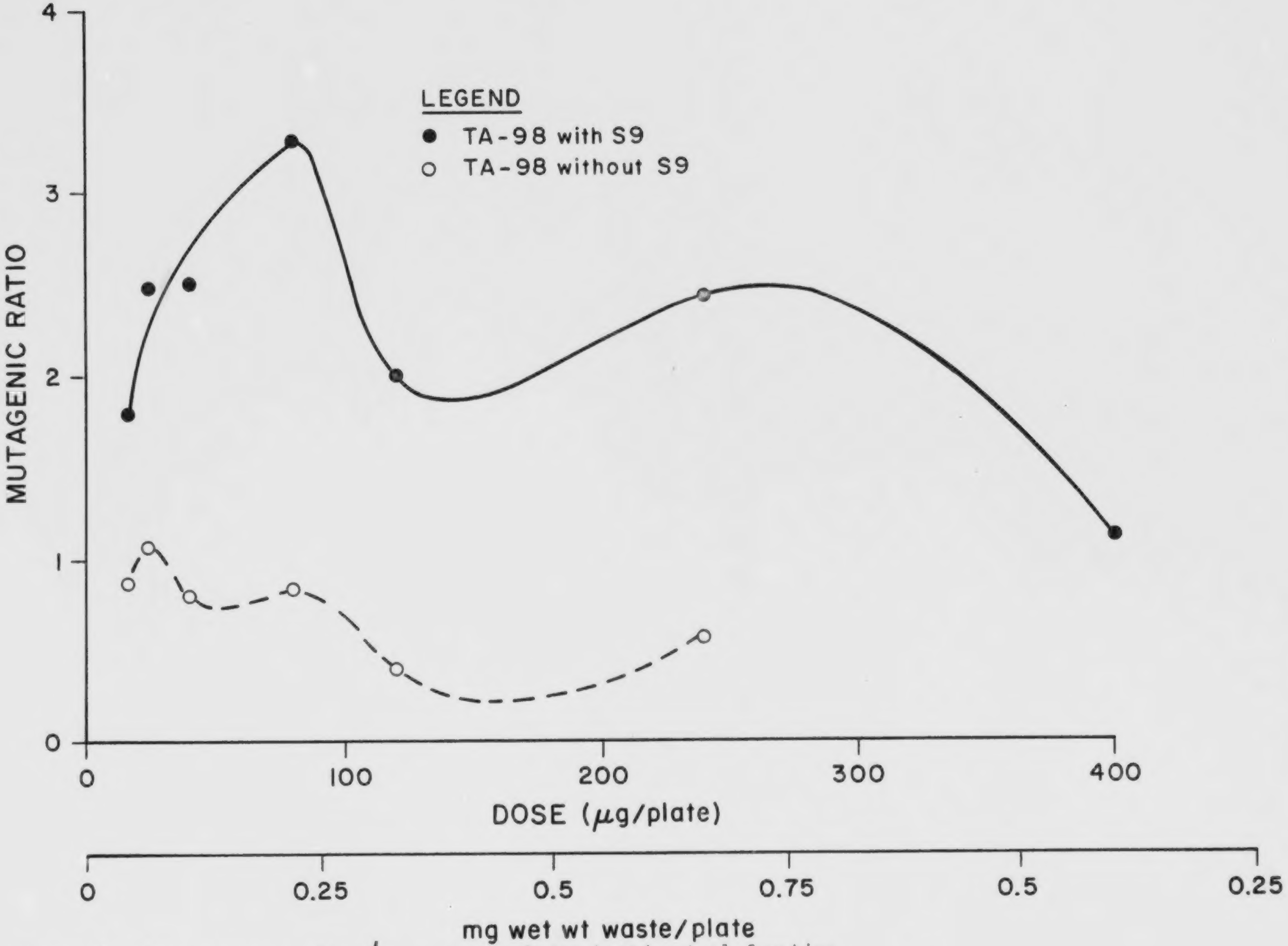

Figure 5. Ames assay results for creosote sludge base/neutral fraction.

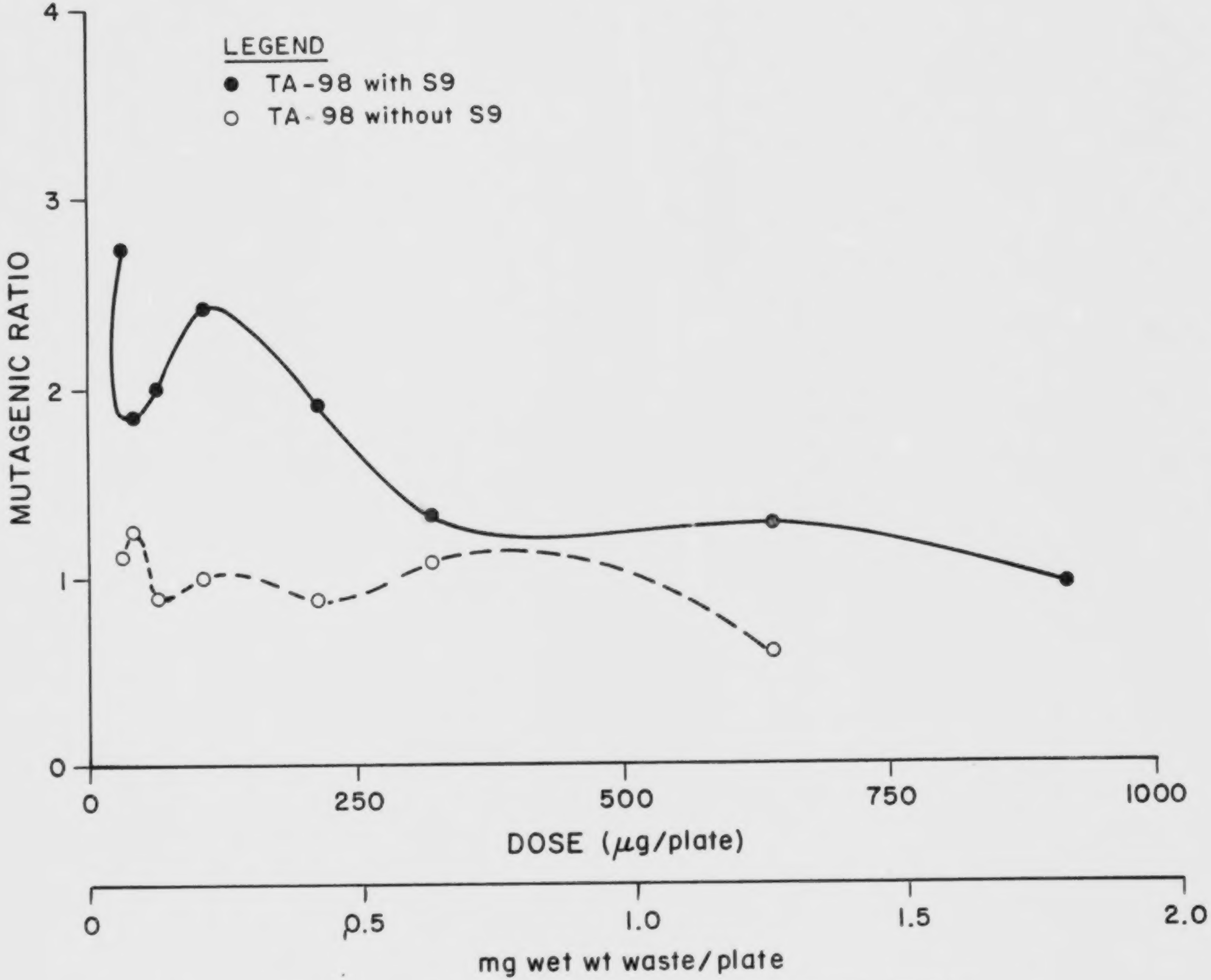

Figure 6. Ames assay results for pentachlorophenol sludge base/neutral fraction.

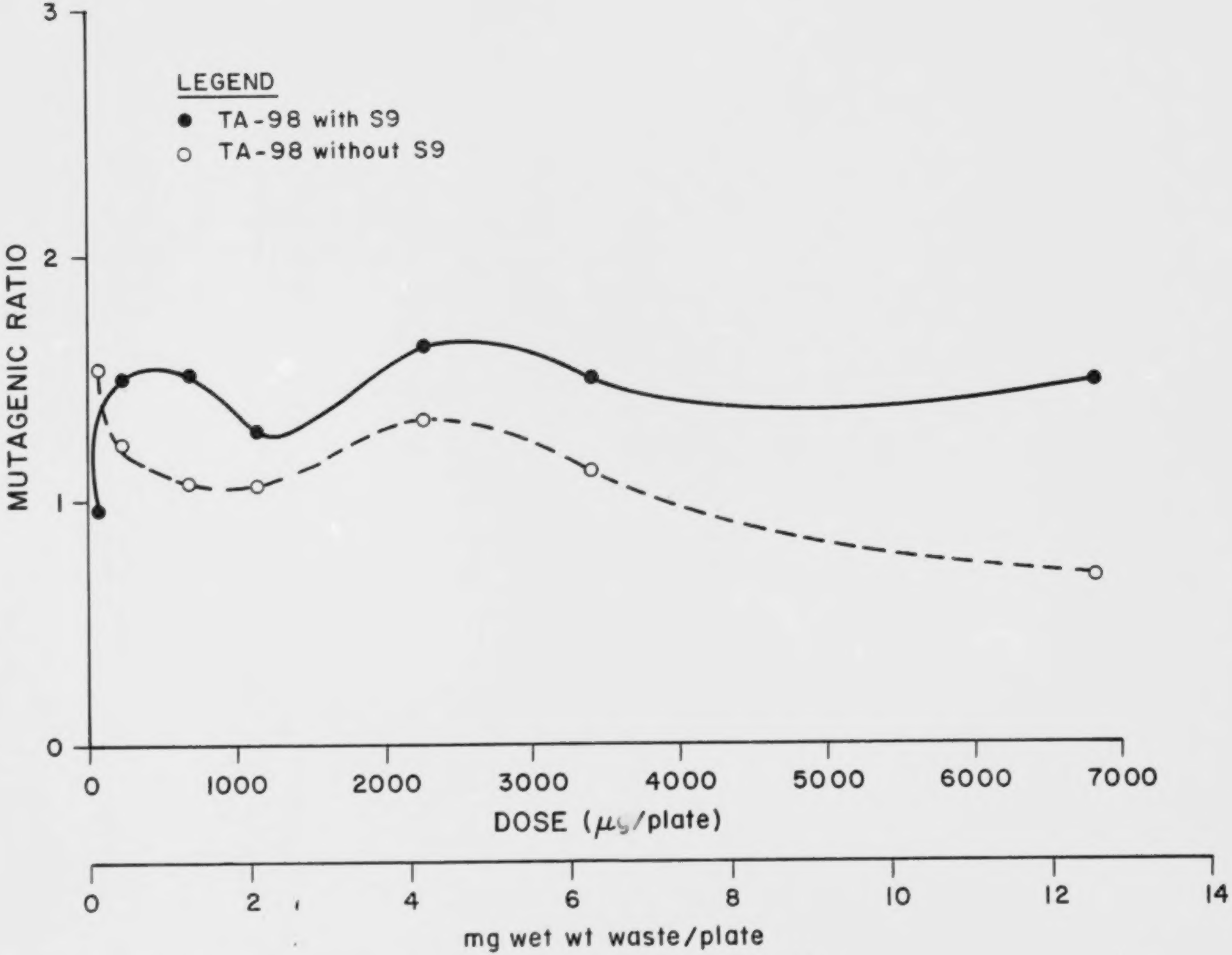

Figure 7. Ames assay results for pentachlorophenol sludge acid fraction.

exhibited. The background lawn showed signs of toxicity to the bacteria at the 641 μg/plate dose, with increased toxicity evident with larger doses. No mutagenicity was detected for the acid fraction of the PCP waste either with or without S9 activation (Figure 7). Some indication of toxicity was present at the highest dose (6820 μg/plate).

Results of mutagenicity testing on the base/neutral fraction of the API separator sludge are presented in Figure 8. No mutagenicity and no toxicity were indicated at any of the doses tested.

Figure 9 shows Ames assay results for the base/neutral fraction of slop oil emulsion solids. Generally no mutagenicity is evident for the fraction either with or without added S9. Toxicity to the bacteria was definitely observed at 1485 μg/plate dose. For this reason, the mutagenic ratio at this point, 1.88, should not be taken as an indication of a trend toward mutagenicity. Toxicity was initially indicated at a dose of 297 μg/plate in waste samples without addition of S9.

None of the wastes tested showed potential for mutagenicity without S9 activation. All of the wastes, with the exception of API separator sludge, showed low level mutagenic responses with addition of the S9 microsomal mix. Toxicity was generally present to varying degrees in all of the samples except for the base/neutral fraction of the separator sludge.

SOIL CHARACTERIZATION

Introduction

Critical to an evaluation of the soil treatability of a hazardous waste is an understanding of the soil that will act as the treatment medium for the waste. Therefore, soil characterization tests were conducted to obtain specific physical and chemical properties for the two experimental soils. The two soils included Durant clay loam and Kidman sandy loam. Criteria for selection of experimental soils included: 1) general suitability for land treatment of waste (U.S. EPA 1983, 1986b), and 2) differences in physical and chemical properties to allow for evaluation of the potential influence of soil type on waste treatment.

Soil physical and chemical parameters measured were those identified as potentially influencing degradation, transformation, or immobilization of hazardous constituents in soil systems (U.S. EPA 1983, 1984f, 1986b). Physical properties are those characteristics, processes, or reactions of a soil caused by physical forces. Physical properties that were evaluated are given in Table 44. Chemical reactions that occur between waste constituents and the soil must be identified and evaluated with respect to treatment effectiveness. Chemical properties that were evaluated are also given in Table 44.

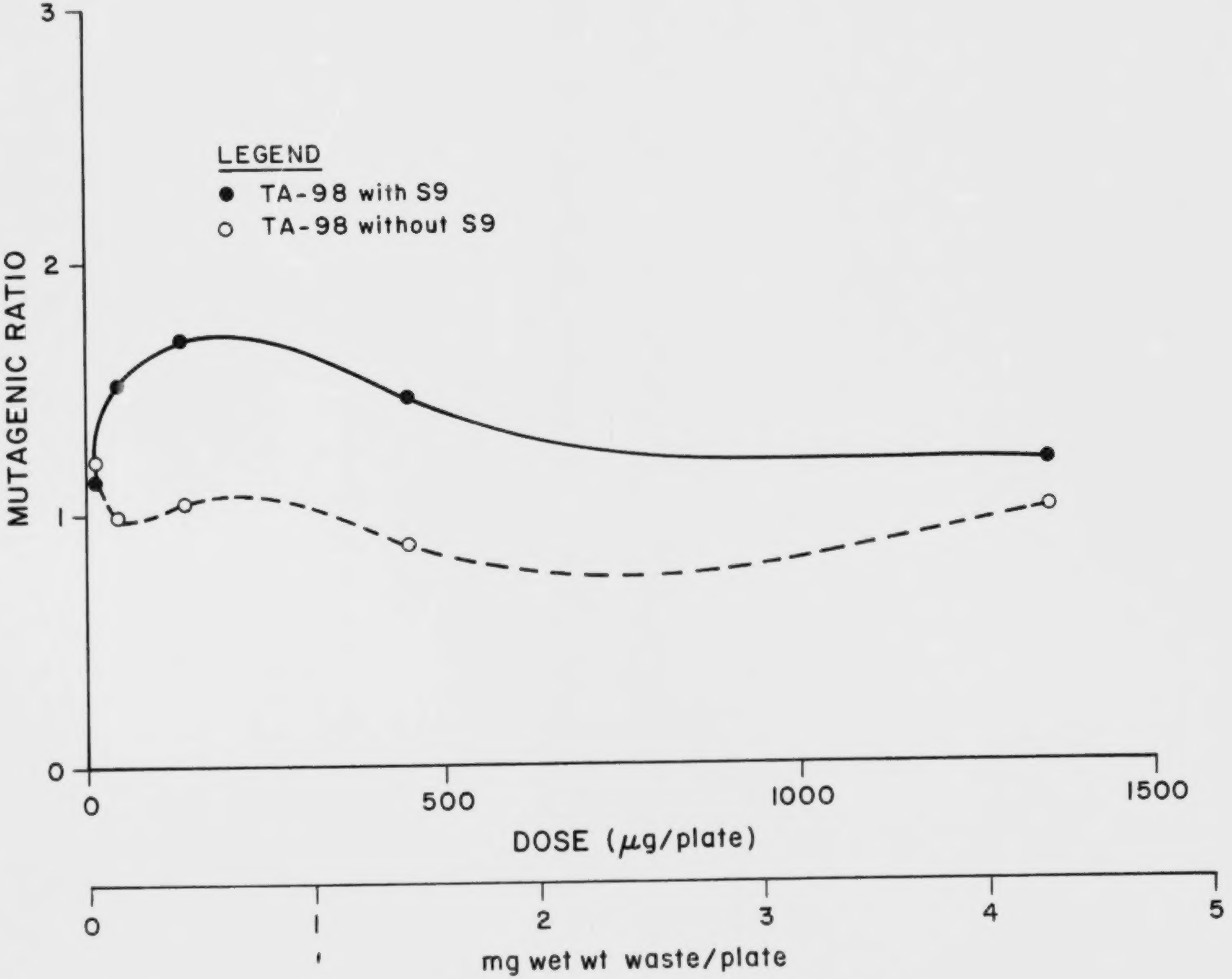

Figure 3. Ames assay results for API separator sludge base/neutral fraction.

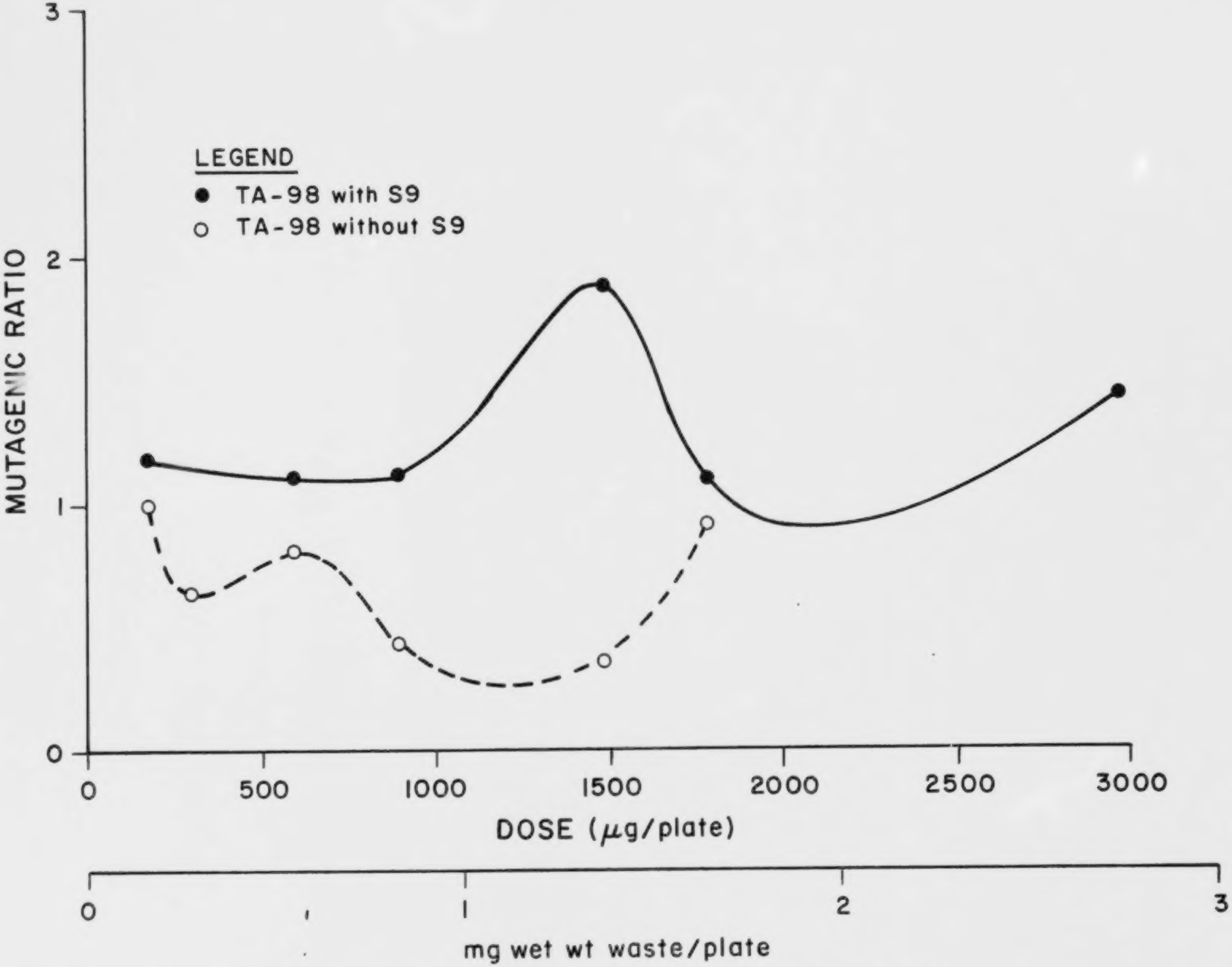

Figure 9. Ames assay results for slop oil emulsion solids base/neutral fraction.

TABLE 44. SOIL PHYSICAL AND CHEMICAL PROPERTIES EVALUATED FOR SOIL CHARACTERIZATION

Soil Physical Properties	Soil Chemical Properties
Soil texture	Cation exchange capacity
Bulk density	Total organic carbon or organic matter content
Soil characteristic curve	Nutrients
Available water capacity	Electrical conductivity
Porosity (saturated water content)	pH
Particle density	Buffering capacity

Specific soil parameters measured and values obtained may be used in quantitative assessment to evaluate treatment and develop management approaches for a soil/waste mixture. An in-depth discussion of the proposed mathematical model to evaluate the effect of site and soil properties on hazardous waste treatment in soil is presented in the Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations (U.S. EPA 1986b).

Materials and Methods

The experimental soils were chosen to represent a spectrum of soil types that are considered suitable for land treatment of wastes. The standard procedures followed for the determination of the parameters listed for each soil are summarized in Table 45. Included for each parameter measured are: 1) standard method reference, 2) instrumentation, and 3) precision and accuracy objectives using the method.

Results and Discussion

Soil physical, chemical and biological parameters measured are presented given in Table 46 for the Durant clay loam and in Table 47 for the Kidman sandy loam. Soil moisture characteristic curves for these soils are given in Figures 10 and 11 for the Durant and Kidman soils, respectively. Soil characteristics that are used in the proposed mathematical model developed by U.S. EPA, RSKERL for evaluating hazardous waste treatment potential in soil are noted in Tables 46 and 47.

An important soil characteristic with respect to waste treatability potential that varied between the two soils was the organic carbon content, which was approximately six times higher in the Durant clay loam than in the Kidman sandy loam. Both soils had active microbial populations, as indicated by soil plate counts.

TABLE 45. MEASUREMENT METHODS AND DATA QUALITY OBJECTIVES FOR SOIL ANALYSES

Parameters	Method	Measurement Method/ Instrumentation	Precision	Accuracy
Particle Size Distribution (Texture)	Chapter 43[*]	Hydrometer method	±10%	Not Applicable
Water Holding Capacity	Chapter 19[*]	Gravimetric	±20%	Not Applicable
Bulk Density	Chapter 30[*]	Core method	±20%	Not Applicable
Soil pH	Chapter 12[+]	Electrometric method; soil suspension/pH electrode	±0.1 units	±0.2 units
Moisture Content	Chapter 7[*]	Gravimetric	±20%	Not Applicable
Total Porosity	Chapter 21[*]	Density method	±20%	Not Applicable
Cation Exchange Capacity (CEC)	Chapter 8[+]	Displacement method	±15%	Not Applicable
Soluble Salts	Chapter 10[+]	Saturation extract; electrical conductivity with conductivity meter	±20%	Not Applicable
Metals	Chapters 2, 16-23[+] 3000 series[#] 7000 series[#]	Extraction; atomic absorption analysis	±10%	±10%
Nitrogen Forms				
NH_4-N	Chapter 33[+] Section 350.2[**] Method 417[++]	Extraction; Nesslerization; titrimetric	±10%	±11%

TABLE 45. CONTINUED

Parameters	Method	Measurement Method/ Instrumentation	Precision	Accuracy
Nitrogen Forms (Cont.)				
NO_2-N, NO_3-N	Chapter 33[+] Section 353.2[**] Method 418[++]	Extraction; automated cadmium reduction	± 5%	±11%
Total Nitrogen	Chapter 31[+]	Micro-Dumas method (combustion method)	± 8%	±12%
Phosphorus Forms				
Ortho-phosphate	Chapter 24[+] Method 424[++]	Extraction; ascorbic acid method	± 6%	± 9%
Total Phosphorus	Chapter 24[+] Method 424[++]	Digestion; ascorbic acid method	± 9%	±12%
Total Organic Carbon	Chapter 29[+] Method 505[++]	Combustion; TOC analyzer	±10%	±15%
Oil and Grease	Section 413.1[**] Method 503[++]	Extraction method for sludge samples	±15%	±18%
Enumeration of Soil Microorganisms				
Bacteria, Fungi	Chapter 37[+]	Total plate counts; spread plate method	±20%	Not Applicable

[*] Methods of Soil Analysis, Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling. C. A. Black, Editor. American Society of Agronomy, Madison, WI (1965).

[+] Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties. Second Edition. A. L. Page (Ed.). American Society of Agronomy, Madison, WI (1982).

[#] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Second Edition, U.S. Environmental Protection Agency, Washington, DC (1982).

[**] Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020, U.S. Environmental Protection Agency, Cincinnati, OH (1979).

[++] Standard Methods for the Examination of Water and Wastewater, Fifteenth Edition, American Public Health Association, Washington, DC (1981).

TABLE 46. CHARACTERIZATION OF DURANT CLAY LOAM SOIL COLLECTED FROM PROPOSED U.S. EPA LAND TREATMENT RESEARCH FACILITY, ADA, OKLAHOMA

Soil Characteristic	Value
Physical Properties:	
Bulk density*	1.59 g/cm^3
Texture*	Clay loam
Moisture at	
1/3 atmosphere	41.6%
15 atmospheres	12%
Saturation*	55%
Chemical Properties:	
pH	6.6
CEC	20.5 meq/100g
Organic carbon*	2.88%
Total phosphorus	0.03%
Total nitrogen	0.21%
Nitrate nitrogen	18 ppm
Sulfate in saturated extract	0.3 meq/l
EC of saturated extract	0.5 mmhos/cm
Iron	28 ppm
Zinc	3.8 ppm
Phosphorus (bicarbonate extractable)	3.0 ppm
Potassium	177 ppm
Ammonium acetate-extractable cations	
Sodium	0.2 meq/100g
Potassium	0.7 meq/100g
Calcium	19.4 meq/100g
Magnesium	4.7 meq/100g
Water soluble cations	
Sodium	0.03 meq/100g
Potassium	0.01 meq/100g
Calcium	0.21 meq/100g
Magnesium	0.08 meq/100g
Biological Properties:	
Soil plate counts	
Bacteria	5.1 x 10^7/g
Fungi	2.6 x 10^5/g

*Soil properties required for use in modeling land treatment of hazardous waste (U.S. EPA 1986b).

TABLE 47. CHARACTERIZATION OF KIDMAN SANDY LOAM SOIL COLLECTED FROM USU AGRICULTURAL EXPERIMENT FARM AT KAYSVILLE, UTAH

Soil Characteristic	Value
Physical Properties:	
Bulk density*	1.49 g/cm^3
Texture*	Sandy loam
Moisture at	
1/3 atmosphere	20%
15 atmospheres	7%
Saturation*	24%
Soil Classification:	Typic Haplustoll
Chemical Properties:	
pH	7.9
CEC	10.1 meq/100g
Organic carbon*	0.5%
Total phosphorus	0.06%
Total nitrogen	0.07%
Nitrate nitrogen	3.7 ppm
Sulfate in saturated extract	4.8 ppm
EC of saturated extract	0.2 mmhos/cm
Iron	9.0 ppm
Zinc	1.2 ppm
Phosphorus (bicarbonate extractable)	27 ppm
Potassium	117 ppm
Ammonium acetate-extractable cations	
Sodium	0.24 meq/100g
Potassium	0.42 meq/100g
Calcium	13.6 meq/100g
Magnesium	1.7 meq/100g
Water soluble cations	
Sodium	0.01 meq/100g
Potassium	<0.01 meq/100g
Calcium	0.04 meq/100g
Magnesium	0.01 meq/100g
Biological Properties:	
Soil plate counts	
Bacteria	6.7 x 10^6/g
Fungi	1.9 x 10^4/g

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*Soil properties required for use in modeling land treatment of hazardous waste (U.S. EPA 1986b).

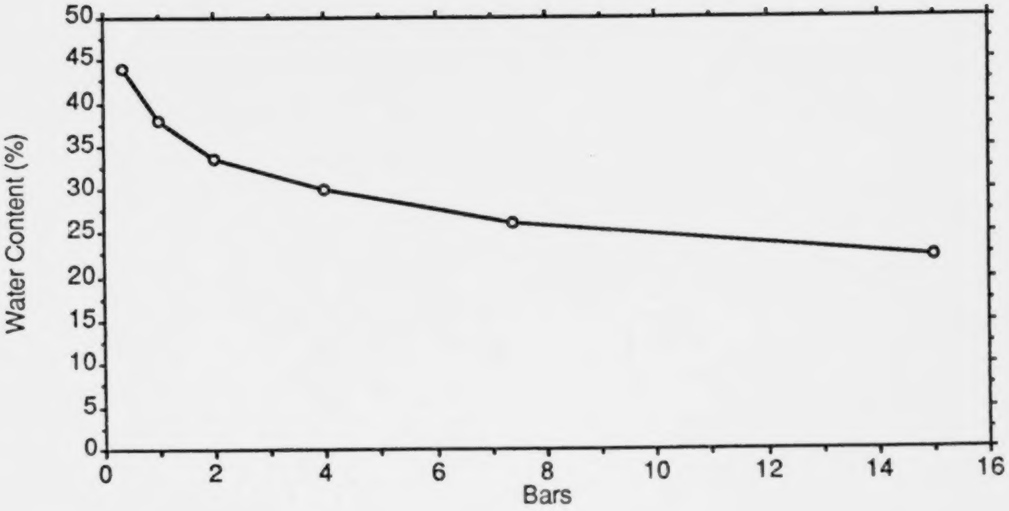

Figure 10. Soil moisture characteristic curve for Durant clay loam.

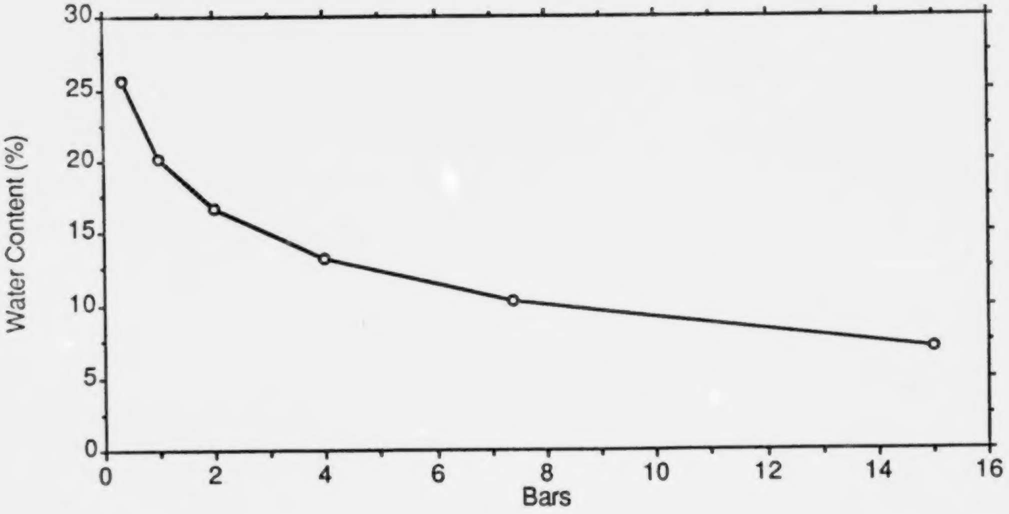

Figure 11. Soil moisture characteristic curve for Kidman sandy loam.

WASTE LOADING RATE EVALUATION

Introduction

Determination of acceptable waste application rates (mass/area/application) is specifically identified in federal HWLT regulations (40 CFR Part 264.272) as a requirement for conducting a land treatment demonstration (LTD). Since the decomposition of a hazardous waste and the detoxification of organic waste constituents in the soil depend to a large extent on biological activities of soil microorganisms, an important consideration in determining waste application rates is the potential impact of the waste on microbial activity. This impact may be measured using a battery of short-term bioassays that measure acute toxicity.

Possible Assays--

Appropriate bioassays should reflect the activity and/or survival of the soil microbial population. This information may indicate potential effects on the microbes responsible for waste degradation. The tests selected should be sensitive enough to indicate potential adverse impacts of a candidate waste on the soil microbial population, which is directly related to the assimilative capacity of the soil. Soil may be acclimated through additions of low concentrations of some wastes (e.g., pentachlorophenol waste) so that the toxicity of successive waste applications to the degradative populations is minimized. Assays used to determine toxicity in acclimated soils should reflect the response of the general microbial community (e.g., respiration) and may be designed to measure specific degradative activity (e.g., dechlorination) to waste addition. The objective is to predict initial loading rates that will allow detoxification of hazardous constituents to occur within the defined waste treatment soil as a result of normal soil biotransformation processes.

The toxicity screening tests to be used should be easily performed, rapid, and inexpensive. The tests also should be validated for the ability to demonstrate responses of the soil microbial population to toxic environments.

Materials and Methods

Microtox--

The Microtox^{TM} system is a simple standardized toxicity test system which utilizes a suspension of marine luminescent bacteria (Photobacterium phosphoreum) as bioassay organisms (Bulich 1979). The system measures acute toxicity in aqueous samples. An instrumental approach is used in which bioassay organisms are handled like chemical reagents. Suspensions with approximately 1,000,000 bioluminescent organisms in each are "challenged" by addition of serial dilutions of an aqueous sample. A temperature controlled photometric device quantitatively measures the light output in each suspension before and after addition of the sample. A reduction of light output reflects physiological inhibition, thereby indicating the presence of toxic constituents in the sample.

For evaluation of waste loading rates, acute toxicity tests are conducted using the water soluble fraction (WSF) extracted from appropriate samples of waste, soil and/or a series of waste-soil mixtures. An EC50 (effective concentration causing a 50 percent decrease in bacterial bioluminescence (Beckman Instruments 1982)) is calculated for each WSF extracted. Results are used to calculate the range of loading rates that will not effect an unfavorable impact on soil microbial detoxification potential.

The small volume of sample required (as little as 10 ml) and the rapidity in which results can be obtained (less than 1 hour for the assay itself) are highly desirable features of a screening procedure. Another attractive feature of this bacterial bioluminescence assay is its reported effectiveness in determining relative acute toxicity of complex effluents containing toxic organic constituents (Qureshi et al. 1982; Vasseur et al. 1984; Burks et al. 1982; Casseri et al. 1983; and Indorato et al. 1984). In each of these studies, Microtox^{TM} results were compared with those from several other assays and found to provide a reliable indication of the presence of toxic organics. Both Qureshi et al. and Vasseur et al. reported Microtox^{TM} to be more sensitive to complex organic effluents than the other assays tested. King (1984) reported that the production of light by the luminescent bacteria in the Microtox^{TM} reagent is very sensitive to the presence of inhibitory chemicals.

Strosher (1984) reported the assay to be a viable method of screening for apparent toxicity in complex waste drilling fluids. Microtox^{TM} results were found to correlate closely with those from rainbow trout bioassays. Strosher recommended that this assay be utilized as a tool in evaluating effects of drilling fluids on soils. In an earlier paper on the subject, Strosher et al. (1980) reported that small changes in concentrations of toxic components could be detected using the Microtox^{TM} procedure.

Microtox^{TM} toxicity screening test results have been used by several researchers to establish a range of initial waste application rates that will not result in undesirable impacts on the soil system with respect to treatment potential, thereby allowing detoxification of hazardous organic constituents to occur (Matthews 1983; Matthews and Bulich 1986; Sims 1985; and Matthews and Hastings 1985).

King (1984) reported Microtox^{TM} to be more sensitive to inhibitory chemicals than activated sludge organisms. Slattery (1984) found that when the influent EC50 for Microtox^{TM} became less than 10 percent, activated sludge organisms became completely inactive. The Microtox^{TM} test should be usable for predicting initial waste application rates if a similar relationship exists between the inhibition of Microtox^{TM} bioluminescence and soil microbial activity.

Experimental Apparatus--

A tumbler, wrist-action or platform shaker is used to extract the WSF from each sample. Following extraction, the Microtox^{TM} system is used to determine the relative residual acute toxicity in each WSF sample.

Water Soluble Fraction (WSF) Extraction Procedure--

A slight modification of the distilled, deionized water (DW) extraction procedure as described by Matthews and Bulich (1986) is used to generate WSF samples. The following steps are followed to prepare these samples for toxicity testing:

a. Place a 100 g sample of each of the background soil, waste, and selected soil-waste mixtures into a glass extraction vessel.

b. Add 400 ml of distilled, deionized water (4:1 vol/wt extraction ratio) to each vessel and seal tightly.

c. The tumbler shaker is the method of choice for mixing. If a wrist-action shaker is used, place the vessels on the shaker at a 180^{0} angle; if a platform shaker is used, place the vessels on their side. In all cases, the extraction vessels must be sealed tightly.

d. Allow the extraction vessels to shake for 20 $\underline{+}$ 4 hrs at approximately 30 rpm in the tumbler shaker or 60 rpm on the wrist-action or platform shaker.

e. Following the specified mixing period, remove flasks from the shaker and allow them to sit for 30 minutes. Decant the supernatants into high-speed centrifuge tubes. Add 0.4 g of NaCl for each 20 ml of sample; shake; then centrifuge at 2,500 rpm for 10 minutes.

f. Prepare a sample from each test unit for Microtox^{TM} testing by pipetting 20 ml of elutriate from each centrifuge tube into a clean glass container, sealing and storing at 4^{0}C. Care must be taken to ensure that any floating material is not transferred. As soon as all samples are prepared, begin Microtox^{TM} testing; conduct all tests the same day that they are prepared.

g. Follow the test procedure outlined in the Microtox^{TM} System Operating Manual (Beckman Instruments, Inc. 1982).

Data Interpretation--

Relative acute toxicity values (EC50 value along with upper and lower 95 percent confidence limits) are calculated for each WSF extract. This involves preparing a log-log plot of concentration versus gamma light decrease (gamma is the ratio of light loss to light remaining), corrected for effects of light drift based on a blank response. The concentration of the sample corresponding to a gamma light decrease of 1 is termed the EC50 (t,T), meaning it caused a 50 percent decrease in light output at exposure time (t) and test temperature (T).

Soil Respiration--

Soil respiration is generally accepted as a measure of overall soil microbial activity (Hersman and Temple 1979) and has been used as an indicator of the toxicity or of the utilization of organic compounds added to the soil environment (Pramer and Bartha 1972). Respiration may also act as an indicator for microbial biomass in soil because the transformations of the important organic elements (C,N,P, and S) occur through the biomass (Frankenberger and Dick 1983). Measurement of CO_2 evolution from soil samples is a commonly used indicator of soil respiration, although measurement of O_2 uptake using a Warburg-type respirometer is a viable alternative for short-term respiration. Evolution of CO_2 can be measured in flow-through or enclosed systems. Flow-through systems involve passing a stream of CO_2-free air through the incubation chamber and then capturing CO_2 from the effluent gas stream in alkali traps (Atlas and Bartha 1972). The Biometer flask described by Bartha and Pramer (1965) is an example of the enclosed system. It consists of an Erlenmeyer flask modified with a side-arm addition which serves as an alkali reservoir for trapping CO_2. A septum in the side-arm allows for removing samples of the alkali. The flask itself is fitted with an ascarite trap for maintenance of CO_2-free aerobic conditions within the container. The carbon dioxide produced by microbial respiration is quantitated by titration of the alkaline solution with acid of known normality or by determination of total inorganic carbon in the solution through use of a carbon analyzer.

Determination of soil respiration through CO_2 evolution is an inexpensive and simple method for indicating general soil microbial activity and acute effects of added substrates on that activity. Description of the use of soil respiration in the literature is widespread, indicating the general acceptance of respiration as an indicator of soil microbial activity. Soil respiration is limited in that results will not necessarily reflect changes in specific types and groups of microorganisms nor will it reflect the potential for anaerobic degradation or degradation of specific organic constituents.

Experimental Apparatus--

Each experimental unit consists of a 500 ml Erlenmeyer flask having a one-hole stopper fitted with an ascarite trap. A stiff wire bent to an 'L' shape at the bottom is suspended from the stopper. A scintillation vial attached to the wire with a rubber band contains 0.5 N KOH for capturing CO_2 released from the soil.

Experimental Procedure--

The method recommended below is modified from the procedure described by Bartha and Pramer (1965).

a. Distribute 50 g of each of the background soil, waste, and soil:waste mixtures to 500 ml flasks, with triplicates for each loading. Also include three empty flasks as blanks.

b. Place a scintillation vial filled with 15 ml of a 0.5 N solution of KOH into each flask and secure the stoppers.

c. Incubate the flasks at room temperature (22 ± 1°C).

d. Monitor the evolution of CO_2 for a 24-hour period. For determination of detoxification potential, CO_2 evolution will be monitored at specific time intervals.

e. The alkali traps are changed by removing the vial of KOH from each flask, capping it, and replacing the vial with one freshly filled with alkali.

f. Determine the amount of CO_2 in each trap using a carbon analyzer and testing for total inorganic carbon. Where a carbon analyzer is not available, the amount of CO_2 evolved can be determined titrimetrically. Add an excess of $BaCl_2$ to the alkaline solution to precipitate the carbonate as insoluble $BaCO_3$. With phenolphthalein as an indicator, titrate the unreacted KOH with 0.6 N HCl. Calculate evolved carbon expressed as CO_2-C, using the following formula (Stotzky 1965):

mg CO_2-C = (ml of HCl to titrate blanks) - (ml of HCl to titrate sample) x normality of HCl x equivalent weight; equivalent weight = 6 if data expressed in terms of carbon.

g. Subtract the mean amount of CO_2-C found in the blank flasks from the mean of the results from the other flasks. This accounts for the CO_2 which enters the flasks when samples are taken and the flasks are aerated.

h. Check the moisture content of each unit once a week. The availability of water may have a large effect on microbial activity.

Dehydrogenase Activity--

Dehydrogenation is the general pathway of biological oxidation of organic compounds. Dehydrogenases catalyze the oxidation of substrates which produce electrons able to enter the electron transport system of a cell (ETS). Measurement of dehydrogenase activity in soils has been recommended as an indicator of general metabolic activity of soil microorganisms (Frankenberger and Dick 1983; Skujins 1973; Casida 1968). Free dehydrogenases in soil are not expected because cofactors such as NAD and NADH are required, linking dehydrogenase activity to living organisms (Skujins 1978). The type and quantity of carbon substrates, both present and introduced, will influence dehydrogenase activity (Ladd 1978; Casida 1977).

The soil dehydrogenase assay involves the incubation of soil with 2,3,5-triphenyltetrazolium chloride (TTC) either with or without added electron-donating substrates. The water-soluble, colorless TTC intercepts the flow of electrons produced by microbial dehydrogenase activity and is reduced to the water-insoluble, red 2,3,5-triphenyltetrazolium formazan (TTC-formazan). The TTC-formazan is extracted from the soil with methanol and quantified colorimetrically.

The soil dehydrogenase activity assay is simple and efficient. It is also a convenient test to run since the only major pieces of equipment required are a spectrophotometer, a centrifuge, and depending on selected test conditions, an incubator. However, since the assay indicates general activity of the major portion of the soil microbial community, it may not reflect effects of an added substrate or toxicant on specific segments of the community.

Experimental Apparatus and Procedure--

The method for determination of dehydrogenase activity is based on Klein et al. (1971). Activity both with and without glucose addition is determined. Sorensen (1982) found that the increase in soil dehydrogenase activity due to glucose addition can be more sensitive to stress than the activity without glucose.

Triplicate test units are prepared for each of the background soil, waste, and soil:waste mixtures. Color correction is accomplished by preparing one extra tube for each combination of soil:waste mixture with or without glucose and not including TTC.

For each sample:

a. Weigh 2 g soil into each of two 16 x 150 mm culture tubes.

b. Add 0.4 ml of a 4 percent (w/v) solution of triphenyltetrazolium chloride (TTC) to each tube.

c. Into one tube add 1 ml deionized water. To the other tube add 1 ml 0.5 percent glucose.

d. Mix the tubes on a vortex mixer, place stoppers in the tubes, and incubate at 35°C for 22 ± 2 hours.

e. Add 10 ml methanol to each tube. Shake the tubes vigorously for 1 min to extract the red-colored TTC-formazan. Allow the tubes to sit overnight, then shake again for 1 min and centrifuge at 600 x g for 10 min.

f. Read the absorbance of the supernatant from each sample at 485 nm using a 1 cm light path with methanol as a blank.

g. Determine dehydrogenase activity from a standard curve derived from TTC-formazan standards of 1, 2, 5, 10, and 20 mg/l in methanol. Calculate color-corrected results by subtracting the absorbance value obtained for each sample having no TTC from corresponding TTC-containing samples. Express results as μg formazan produced per gram dry weight of soil in 24 hours.

Nitrification--

Oxidation of ammonium nitrogen to nitrite and then to nitrate nitrogen is called nitrification. The chemoautotrophic bacteria that derive their energy for growth from the oxidation of ammonium ion (e.g., Nitrosomonas) or nitrite ion (Nitrobacter) are sensitive to environmental stress and are not different from heterotrophic bacteria in the soil in many of their requirements for metabolic activity and growth (Focht and Verstraete 1977). Coupled with the fact the energy yielding substrates and/or oxidized products of nitrification are easily extracted from the soil and measured, the process of nitrification may be used as a bioassay of microbial toxicity in the soil.

A possible disadvantage of using nitrification as a toxicity indicator is the high sensitivity of the bacteria involved. This is especially true of Nitrobacter (Focht and Verstraete 1977). Heterotrophic microbes may be more resistant and resilient.

Experimental Apparatus and Procedure--

The methods outlined below were used by Sorensen (1982) and adapted from Belser and Mays (1980). The intent of the assays is to measure the potential activity of the ammonium or nitrite oxidizing bacteria in the soil over a relatively short period of time, and not to measure the ability of the soil to support growth of these organisms over an extended period. Substrate concentrations are kept low to avoid toxic effects, and to avoid the necessity of dilution prior to nitrite analysis.

Initial potential NH_4^+ oxidation activity procedure--

For each sample:

a. Weigh 6 g of soil into a 125 ml Erlenmeyer flask.

b. Add 25 ml of ammonium-phosphate buffer solution containing 167 mg K_2HPO_4/l, 3 mg KH_2PO_4/l, and 66 mg $(NH_4)_2SO_4$/l. The pH of this solution should be 8 ± 0.2. Note: A buffer close to the test soil pH may be desirable.

c. Add 0.25 ml of 1 M $NaClO_3$ to each flask to block NO_2- oxidation.

d. Cover the flask with aluminum foil and shake on an orbital shaker at 200 rpm for 22 ± 2 h at 24 ± 2°C.

e. Clarify the slurry or portion of the slurry by centrifugation or filtration.

f. Analyze the filtrate or supernatant for NO_2-N (Kenney and Nelson 1982; APHA 1985). Each batch of ammonium-phosphate buffer should also be analyzed for NO_2-N and the concentration subtracted from sample results. Chemical interferences with the Griess-Ilosudy method for MO_2-N are described by Kenney and Nelson (1982) and APHA (1985). Most interferences are uncommon but may occur in some wastes. Oil from petroleum wastes may be present in supernatants and cause difficulties by coating colorimeter cuvets or tubing in automated chemistry apparatus. Oil can usually be removed sufficiently by gravity filtration of the supernatant through medium speed filter paper and removing the filtrate before the last small portion (2-4 ml) of extract, which holds the oil on the surface, passes through the filter.

Initial potential NO_2^- oxidation activity procedure--

a. Weigh 6 g of soil into a 125 ml Erlenmeyer flask.

b. Add 25 ml of nitrite-phosphate buffer solution containing 167 mg K_2HPO_4/l, 3 mg KH_2PO_4/l, and 4.5 mg $NaNO_2$/l. The pH of this solution should be 8 ± 0.2. Note: A buffer close to the test soil pH may be desirable.

c. Add 5 1 of a 20 percent solution of nitropyrin (2-chloro-6-(trichloromethyl) pyridine) in dimethyl sulfoxide to each flask to block the oxidation of indigenous NH_4^+ to NO_2- (Shattuck and Alexander 1963).

d. Process each flask and its contents as described for NH_4^+ oxidation described above in steps d through f. In this case the NO_2-N concentration in the nitrite-phosphate buffer is the initial substrate concentration, and substrate usage is monitored.

Soil Plate Counts--

Total counts of major microbial groups in the soil are intended to show the viability of the soil microbial community. Comparison of counts made before and after waste addition provide an indication of acute microbial toxicity to the specific microbial groups and show the effect on the community as a whole. Dominant species may be suppressed, allowing for an increase in the predominance of less common groups. The change in community structure may be short-lived, but could possibly continue for a lengthy period of time.

Ideally, the plate count procedures should create optimal conditions for the microorganisms to be enumerated; therefore medium composition, incubation conditions and length of incubation are important considerations in plate count assays. It is improbable that all types of microorganisms present in the soil will be detected using agar plates, since all media types are selective to a certain extent (Greaves et al. 1976). Another disadvantage of the plate count assay is that comparisons made among enumerations performed at different times will be accurate only if test conditions for each set of counts are identical. In addition, the plate count method is not conducive to counting numbers of filamentous organisms or those producing large quantities of spores. Also, there is not necessarily any correlation between numbers of microorganisms and measured metabolic activities (Greaves et al. 1976). The microbial life forms suggested for enumeration, total bacteria, actinomycetes and fungi, are the most important soil organisms effecting biological degradation and transformation of hazardous waste constituents.

Media Preparation--

The following three media are recommended for determining viable counts of the selected microbial types: tryptic soy agar for bacteria, Martin's rose bengal media for fungi, and starch-casein agar for actinomycetes. Details on preparation of these media may be found in Wollum (1982).

Experimental Procedure--

a. Prepare a sufficient quantity of plates of each media type.

b. Prepare dilutions of the control soil and each soil:waste mixture in triplicate according to section 4.2.2 of Wollum (1982). Three dilutions of each replicate will be plated on each type of media. For bacteria and actinomycetes 10^{-6}, 10^{-5}, and 10^{-4} dilutions are recommended. For fungi, the suggested dilutions are 10^{-5}, 10^{-4}, and 10^{-3}. The solutions to be used should encompass the optimum number of organisms for counting, i.e., 30-300 colonies for bacterial and actinomycete plates and 10-20 for fungal plates. All dilutions should be prepared in the same manner since comparisons across treatments will be made.

c. Prepare spread plates according to section 5.2.2 of Wollum (1982).

d. Incubate the plates at a controlled temperature, generally between 24 and 28°C. The period of incubation depends on temperature and growth conditions. For bacteria and fungi 4 to 7 days should be sufficient, while actinomycete plates may have to be incubated 10 to 14 days.

e. Average the number of colonies per plate for each dilution and determine the number of colony-forming units per gram dry weight of soil. Significant differences in numbers of colony-forming units from the control can be determined using statistical tests. A significant reduction in the number of colony-forming units found in the soil treated with waste as compared to control soil indicates the degree of acute toxicity.

Preparation of Waste Soil Mixtures for Bioassays--

If air-dried soil is used, it should be brought to the desired moisture content (minimum 60 percent of the water-holding capacity of the soil, preferably a moisture content that will prove typical for field conditions). The soil is acclimated to the increased soil moisture content for 7 to 10 days to allow for growth of soil microorganisms. After the acclimation period, waste which has been thoroughly mixed is added to the soil at the previously selected loading rates. When small percent loadings are to be tested, i.e., $\leq$ 10 percent, it may be difficult to evenly disperse the waste material in the soil. The use of an organic solvent as a dispersal agent may not be feasible in all cases since some solvents have toxic effects on microbial processes. The following method has proved successful for providing a fairly uniform distribution of small quantities of waste in soil. A soil:waste mixture at a concentration higher than the upper loading rate is prepared using air-dried soil. The waste is incorporated into the soil by mixing on a rotary tumbler for 12 hours at 30 rpm. This soil:waste concentrate can be "diluted" with additional acclimated soil so that the final concentration of waste is equal to the desired loading rate. Soil without waste should be added and mixed into the control using identical procedures as used with soil:waste mixtures.

Use of air-dried soil encourages sorption of volatile constituents, since the presence of water can displace volatile constituents from soil. Although some volatile constituents may be lost from the soil during the mixing process, this preparation process simulates application of waste in field conditions using surface incorporation and mechanical mixing of waste with the soil. An alternative method of waste application should be considered if the goal is to simulate subsurface injection to minimize loss of volatile constituents.

After the waste has been added to the soil and thoroughly incorporated, the soil:waste mixture and control are allowed to incubate 24 ± 2 hours. This incubation allows for acute effects of the waste on soil microbiota to be expressed. After the incubation period, the selected toxicity assays are started. Except for soil plate counts, the assays described in this chapter require 24 hours for incubation or extraction.

Preliminary Loading Rate Investigation--

In order to use any of the previously described acute toxicity tests for determining an appropriate range of waste application rates, a set of initial rates to test should be chosen.

Microtox--

Matthews and Hastings (1985) described a method using the Microtox assay to determine an initial range of waste application rates. The following steps are involved:

a. Obtain a 5 kg sample of the site soil and a 1 kg sample of the waste to be applied. Proper sample collection procedures should be used to insure that characteristics of soil and waste samples are representative of those anticipated at the site.

b. Weigh out two 100 g aliquots of air-dried soil which has been crushed and sieved to 2 mm; weigh out two 100 g aliquots of waste which has been thoroughly mixed.

c. Prepare WSF samples for toxicity testing by extracting aliquots of the duplicate waste and soil samples as described in the Microtox methods section.

d. Conduct Microtox™ tests on each WSF sample prepared as previously described. Experience suggests that if the EC50 for the WSF of a given waste as defined by the Microtox™ system exceeds 25 percent, the EC50 for the WSF of any waste-soil combination will exceed 20 percent and toxicity as measured by the Microtox™ system will not be a significant factor in determining loading rate. This does not preclude use of the test system to determine if toxicity reduction of hazardous organic constituents within the waste-soil matrix is occurring over time.

e. If the soil WSF is nontoxic, i.e., the full strength DW extract effects $\leq$ 25 percent decrease in bacterial bioluminescence, the soil has no apparent residual toxicity. If soil residual toxicity is indicated (> 25 percent decrease in light output in the full strength DW extract), the apparent cause should be determined prior to further testing.

f. Determine four loading rates to be used in subsequent toxicity screening tests according to the following criteria:

1) Calculate the EC50 and 95 percent confidence limits for the waste WSF.

2) Choose the upper limit of the 95 percent confidence interval as the highest loading rate to be used. For example, if the WSF of the waste has an average EC50 of 10 percent and upper and lower 95 percent confidence limits of 12 percent and 8 percent, the highest loading rate would be 12 g of waste per 100 g of soil.

3) Use 1/4, 1/2, and 3/4 of the upper limit as the remaining three loading rates (in percent wet weight waste per dry weight soil) for testing.

g. Weigh out four 300 g samples of prepared soil. Add prescribed amount of waste and mix thoroughly to achieve the four loading rates (wt/wt) determined by the criteria described above.

h. From each of the four samples, remove three 100 g (dry wt) subsamples and place in a flask or bottle for extraction. Discard the remainder of the sample.

i. Extract each of the 12 subsamples with distilled, deionized water according to the procedure described previously and conduct Microtox™ test on the WSF constituents.

j. Calculate the EC50 and 95 percent confidence limits for each waste-soil WSF. Average triplicate values to obtain EC50 and 95 percent confidence limits for each loading rate extracted. Transpose each EC50 value to toxicity units (TU) in soil using the following equation:

$$\text{Soil TU} = \frac{100}{\text{EC50}} \times 4$$

k. Prepare a log-log plot of toxicity units versus loading rates for use in estimating an acceptable initial loading rate window. The interception point for 20 soil TU is the lower loading limit for the window; the upper limit is defined as twice the lower limit. Experimental data generated to date suggest that this is a reasonable window for initial loading.

Other Assays--

When using assays other than Microtox^{TM} for preliminary initial application rate estimation, the following procedure may be useful:

a. Choose three or four loading rates that cover the range from 0 to the maximum rate likely to be used based on mobility, soil hydraulic conductivity effects, anticipated degradation rates, or other criteria. Concentration steps should increase by approximately a factor of 10 (e.g., 0, 0.1, 1, and 10 percent by weight).

b. Perform the selected acute toxicity bioassays on each of the soil:waste mixtures.

c. Beginning at the concentration showing little or no toxicity in step b above, prepare a series of loadings that encompasses the concentration where activity is reduced approximately 50 percent relative to the untreated control. Smaller increments in concentration should be used than in step a. above.

d. Repeat the acute toxicity bioassays. The results of these assays should identify a range of loading rates that are not highly toxic to the soil biota. The potential for these loading rates to allow for detoxification should be determined in a longer term toxicity reduction study.

Selection of Waste Loading Rates--

Giving greater weight to the level of toxicity indicated by assays which indicate activity among a broader spectrum of the microbial population (e.g., respiration and dehydrogenase) or indicating general toxicity (Microtox^{TM}), but considering all assay results, select a range of loading rates that are not likely to inhibit microbial activity but will utilize the apparent assimilative capacity of the soil.

The detoxification potential of soil:waste mixtures loaded at rates determined by results of any of the short-term bioassays previously described can be evaluated with a six-week toxicity reduction study. This information will prove useful in refining the set of loading rates to be used for a long-term land treatment demonstration. Matthews and Bulich (1986) have described a toxicity reduction experiment procedure using the Microtox assay where duplicate samples of waste:soil mixtures loaded at selected rates are sacrificed immediately following waste application and at two-week intervals for a six-week period. At each sampling time (i.e., days 0, 14, 28 and 42) the soil:waste mixtures are extracted with water and analyzed for toxicity on the Microtox system. Soil moisture in the test units is maintained between 40 and 70 percent of the soil moisture holding capacity for the duration of the experiment.

The detoxification potential of a given loading rate is indicated by the changes in acute toxicity of the water extract during the experimental period. A significant degree of detoxification is shown by a toxicity reduction trend with the calculated EC50 for day 42 approaching or exceeding 100 percent.

Data Interpretation--

No single assay of soil microbial activity is likely to indicate the activity or viability of the broad spectrum of soil microorganisms or their functions. Measurements of respiration may represent the activity of the broadest community of microorganisms. When information on the toxicity of a waste or its degradation or transformation products is available from more than one assay, decisions on acceptable levels of toxicity for loading rate determinations or determination of detoxification will be more reliable. Broad spectrum assays (e.g., respiration or dehydrogenase) and general toxicity (Microtox^{TM}) are recommended for inclusion in a any battery of assays, but assays relating to specific subgroups of the microbial community (e.g., nitrification, nitrogen fixation, or cellulose decomposition) may also be considered.

Results from assays measuring universal metabolic activities (e.g., carbon dioxide evolution) or general toxicity (e.g., Microtox^{TM}) should normally be give more weight in decision making, but if other assay results indicate severe toxicity, lower loading rates should be investigated.

Results and Discussion

The bioassays used in this study for determining loading rates included the Microtox system and soil respiration. Using the Microtox system, a series of loading rates were evaluated for each soil and waste combination immediately after waste incorporation into the soil. For some soil:waste mixtures, the process was extended to a six-week toxicity reduction study. Using CO_2 respiration, loading rates for the four wastes mixed with Durant clay loam soil were evaluated for a 60-day period.

Selection of Loading Rates for Creosote Waste--

Toxicity reduction study results for creosote waste mixed with Durant clay loam soil are found in Figures 12 through 14. The tests were performed in triplicate at three separate times, using the same soil and waste samples each time. Results of the three tests are comparable, showing that the 0.25 percent loading became essentially nontoxic after 14 days incubation, and with the exception of trial #2, the 0.5 percent loading became nontoxic after 42 days. The highest loading, 1.0 percent, showed a detoxification trend, but the water-soluble fraction of the soil:waste mixture exhibited a fairly toxic EC50 (average of 3 reps = 27.3, S.D. = 9.7) after 42 days incubation.

Figure 15 illustrates soil respiration results for creosote waste applied to Durant clay loam soil. All waste loadings exhibited greater CO_2 production than the soil control, with production of CO_2 increasing with waste loading. The highest creosote loading, 1.0 percent, did not appear to inhibit respiration activity at any time during the 60 days of incubation.

Based on Microtox and soil respiration results, the loading rates determined for creosote waste mixed with Durant clay loam soil were 0.7 percent, 1.0 percent, and 1.3 percent waste wet weight/soil dry weight.

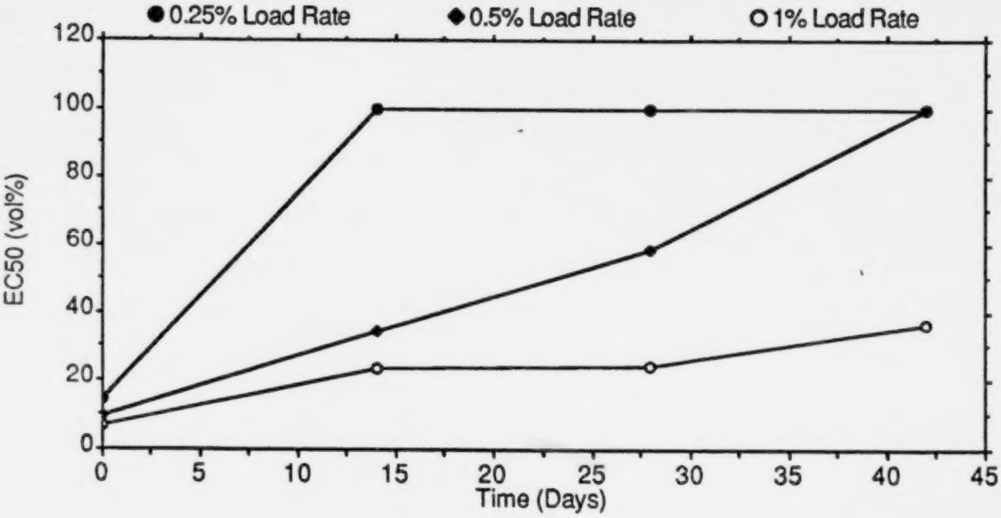

Figure 12. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant clay loam soil for loading rate determination, Trial #1. EC50(5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

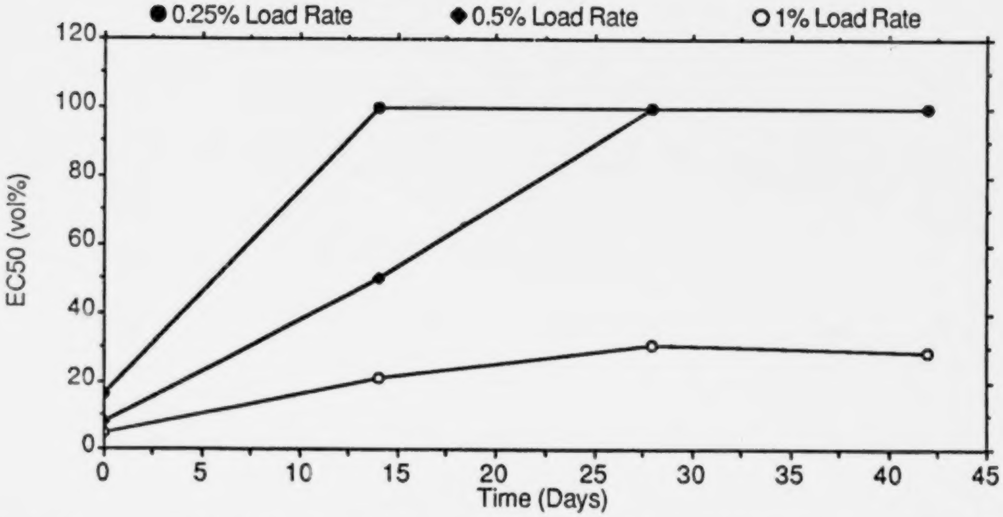

Figure 13. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant lay loam soil for loading rate determination, Trial #2. EC50(5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

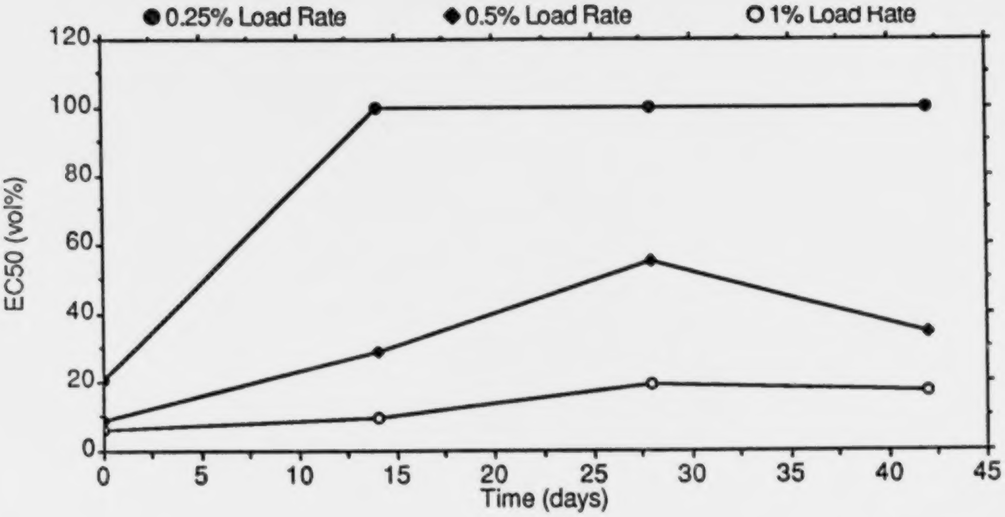

Figure 14. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for creosote waste mixed with Durant clay loam soil for loading rate determination, Trial #3. EC50(5,15^o) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{o}C.

Microtox assay results for creosote waste mixed with Kidman sandy loam soil are presented in Figure 16. Comparison of these results with day 0 results using Durant soil shows that the EC50 values for Kidman soil:creosote mixtures were approximately one-half of those obtained from Durant soil:creosote mixtures. For this reason, the loading rates determined for creosote waste mixed with Kidman soil were less than those for Durant:creosote mixtures. The selected loadings were 0.4 percent, 0.7 percent, and 1.0 percent waste wet weight/soil dry weight.

Selection of Loading Rates for Pentachlorophenol Waste--

The results for the 42-day toxicity reduction study for pentachlorophenol wood preserving waste mixed with Durant clay loam soil (Figure 17) showed detoxification of the waste at the 0.2 percent loading rate after 14 days incubation. A detoxification trend over the 42-day period was present for the 0.4 percent loading, but only slight changes in toxicity were evident at the highest loading, 0.8 percent.

Soil respiration results for Durant:PCP mixtures are presented in Figure 18. Carbon dioxide evolution increases with waste loading, and production of CO_2 for all waste loadings was greater than that of the soil control. Doubling the PCP loading from 0.2 percent to 0.4 percent increased CO_2 production 25 percent by day 55, while doubling the loading again from 0.4 percent to 0.8 percent increased production by only 16 percent.

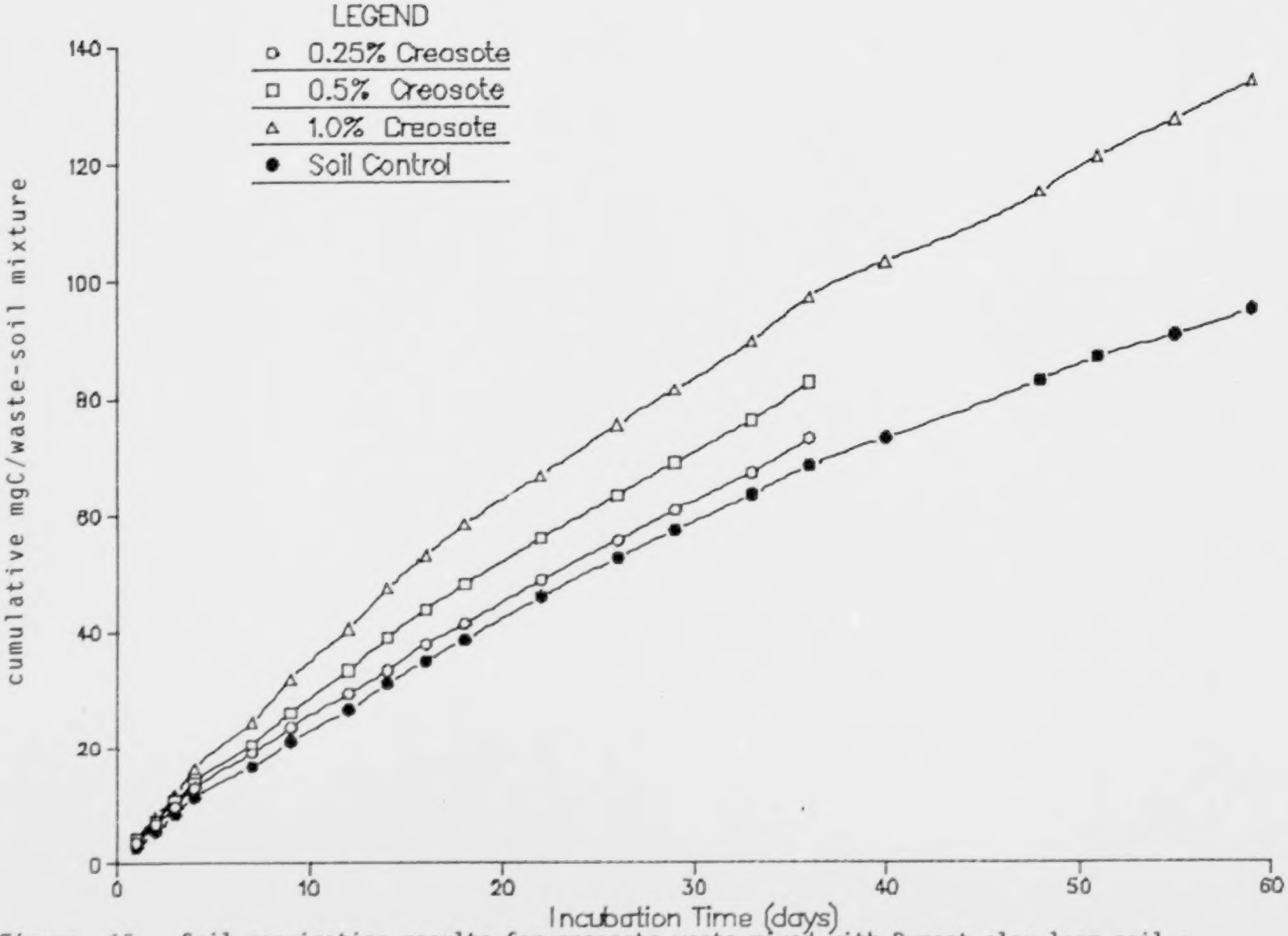

Figure 15. Soil respiration results for creosote waste mixed with Durant clay loam soil.

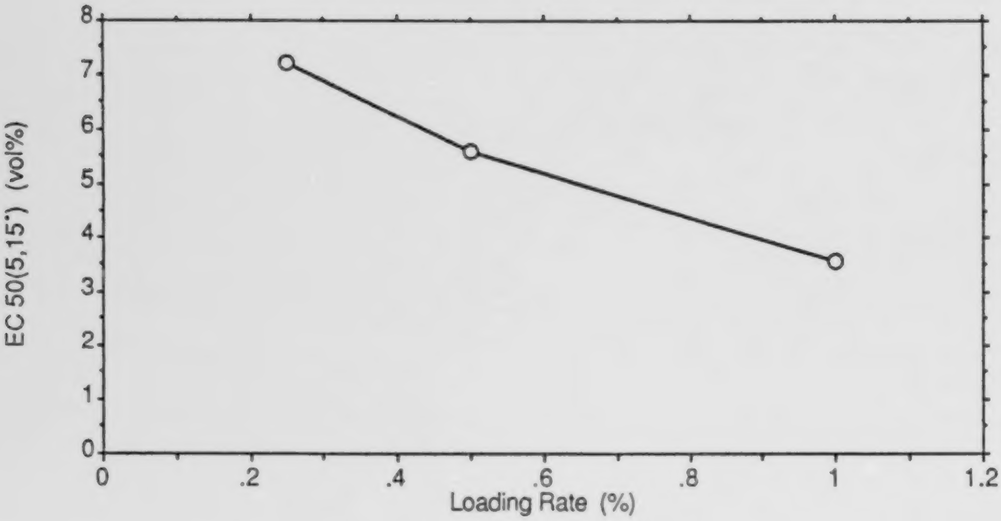

Figure 16. Toxicity of water soluble fraction measured by the Microtox assay for creosote waste mixed with Kidman sandy loam soil for loading rate determination. EC50(5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

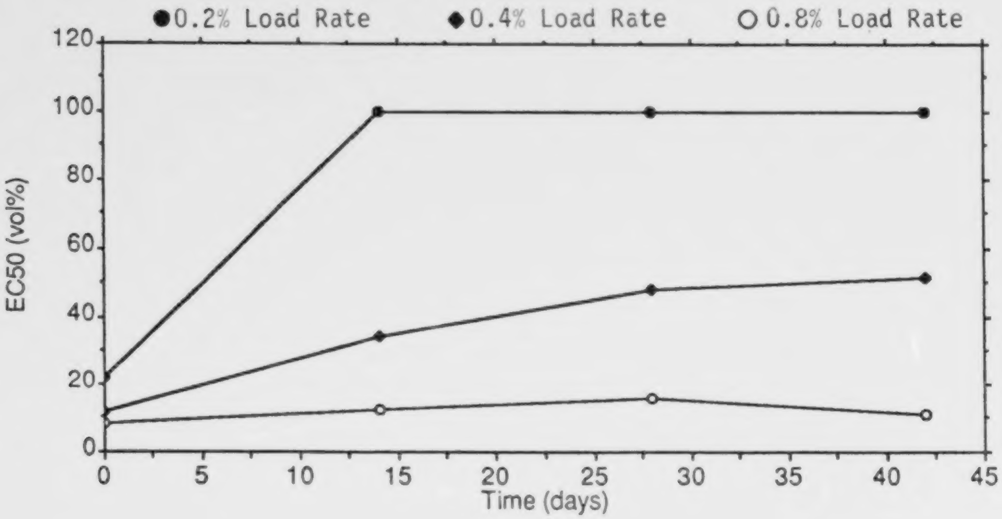

Figure 17. Toxicity of water soluble fraction measured by the Microtox assay with incubation time for PCP wood preserving waste mixed with Durant clay loam soil for loading rate determination. EC50(5,15°) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15°C.

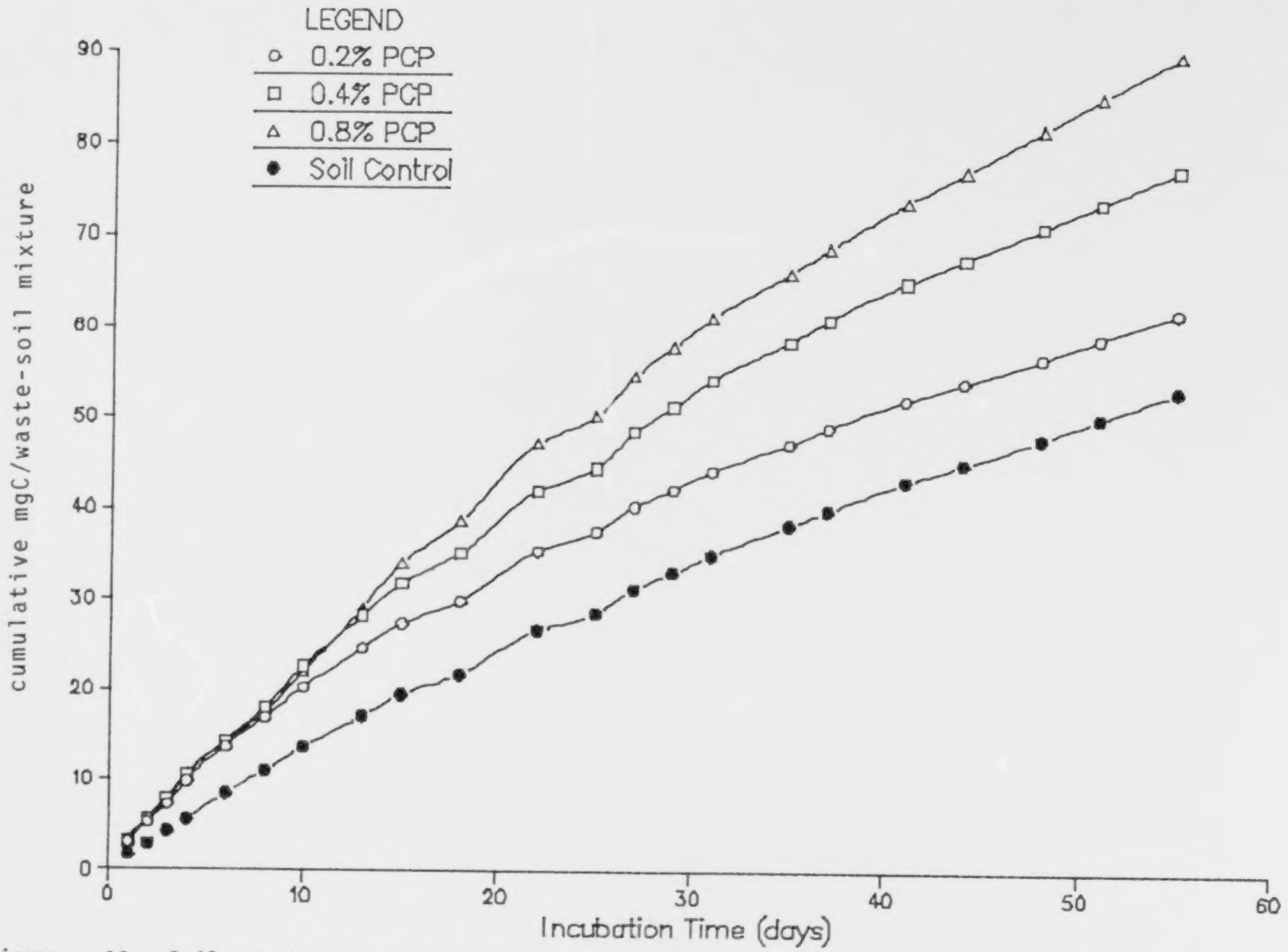

Figure 18. Soil respiration results for PCP waste mixed with Durant clay loam soil.

Therefore, while increased loading rates exerted a toxic effect on the Microtox organism, an obvious toxic effect was not observed with the soil respiration assay. The soil loading rates selected for further study based on Microtox results were 0.3 percent, 0.5 percent, and 0.7 percent waste wet weight/soil dry weight.

Figure 19 presents Microtox results for PCP wood preserving waste mixed with Kidman sandy loam. Aqueous extracts of these soil:waste mixtures at very small percentages of PCP proved highly toxic to the Microtox organism. At the lowest loading tested, 0.05 percent, the resulting extract EC50 was 14.2 percent by volume. A comparable EC50 of 11.6 percent was obtained for the 0.4 percent loading of PCP mixed with Durant clay loam soil, almost a 10-fold increase in waste loading. The loadings chosen for PCP mixed with Kidman sandy loam were 0.07 percent, 0.15 percent and 0.3 percent waste wet weight/soil dry weight.

Selection of Loading Rate for API Separator Sludge--

The toxicity of aqueous extracts of various loadings of API separator sludge mixed with Durant clay loam soil as determined by the Microtox system is shown in Figure 20. These results show no trend toward increasing toxicity with increased waste loading. It appears that the toxicity of this waste as indicated by the Microtox system, was negligible.

Carbon dioxide evolution results for Durant:separator sludge mixtures are presented in Figure 21. Although all loadings increased production of CO_2 over that of the soil control, there was little difference between the loadings. Doubling the loading from 8 percent separator sludge to 16 percent caused essentially no change in CO_2 production again suggesting negligible toxicity and that some resource other than the decomposable components of the waste limited respiration activity when more than 8 percent waste was applied. Perhaps oxygen movement through the soil was hampered as pore space was filled with oil.

Loading rates selected based on the information obtained from Microtox and respiration assays for API separator sludge mixed with Durant clay loam soil were 6 percent, 9 percent and 12 percent waste wet weight/soil dry weight. Twelve percent waste was selected as an upper limit based on current industrial practice, the need for waste retention in the treatment zone, and the lack of respiration stimulation at higher application rates.

Microtox results for API separator sludge mixed with Kidman sandy loam soil are presented in Figure 22. It appears that there may be a trend towards increasing toxicity with increased loading rate. The loading rates for Kidman sandy loam were identical to those chosen for Durant clay loam, 6 percent, 9 percent, and 12 percent waste net weight/soil dry weight.

Selection of Loading Rates for Slop Oil Emulsion Solids--

Microtox water soluble extract toxicity results for slop oil waste applied to Durant clay loam soil are shown on Figure 23. The EC50 of 47.8

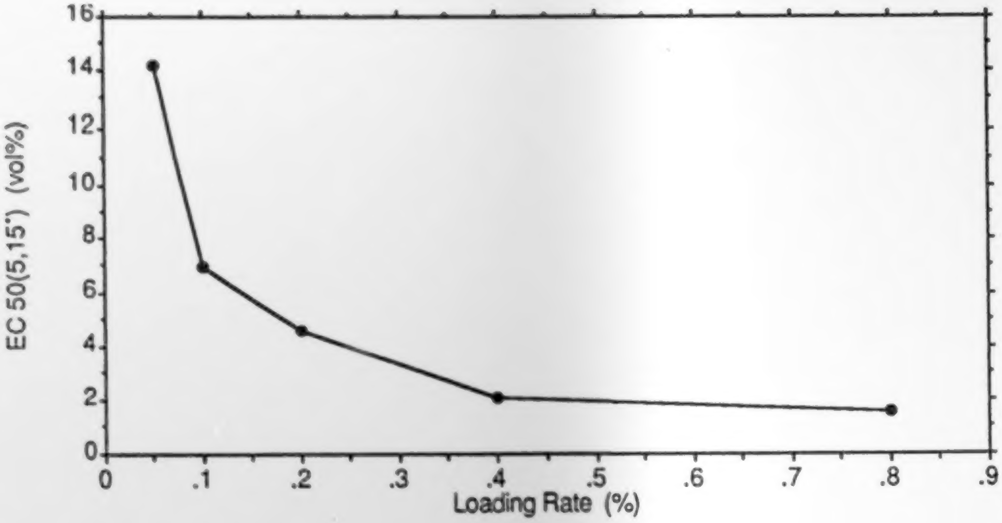

Figure 19. Toxicity of water soluble fraction measured by the Microtox assay for PCP wood preserving waste mixed with Kidman sandy loam soil for loading rate determination. EC50(5,15^{0}) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{0}C.

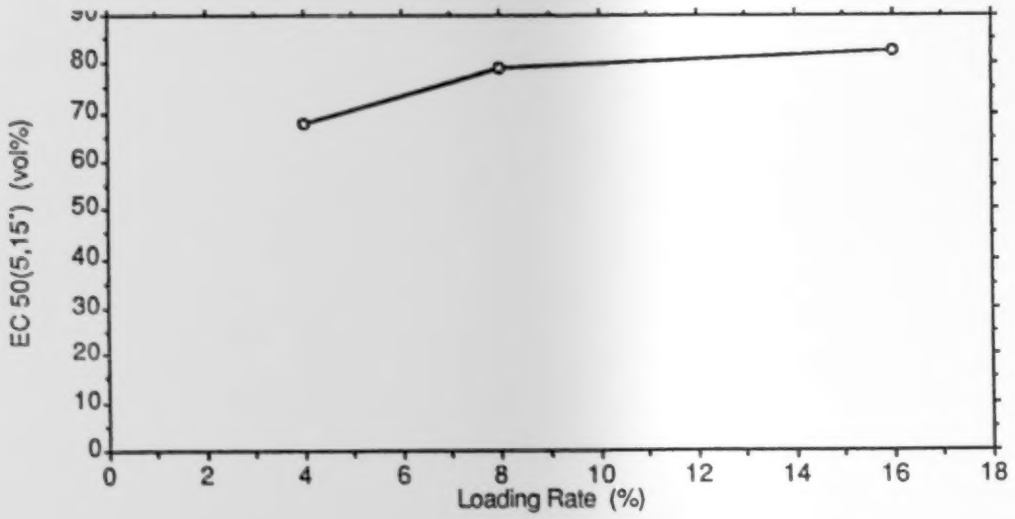

Figure 20. Toxicity of water soluble fraction measured by the Microtox assay for API separator sludge waste mixed with Durant clay loam soil for loading rate determination. EC50(5,15^{0}) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{0}C.

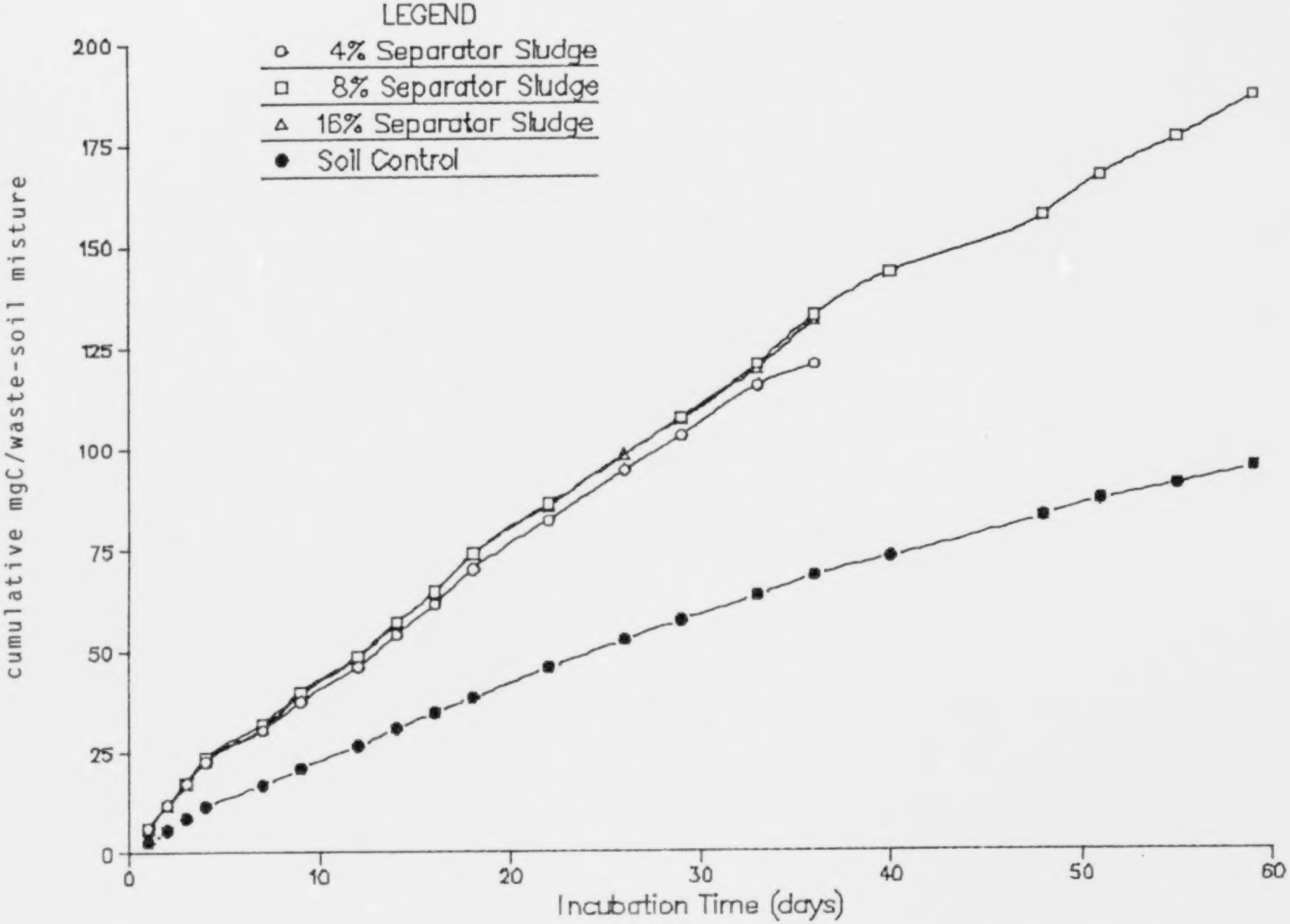

Figure 21. Soil respiration results for API separator sludge mixed with Durant clay loam soil.

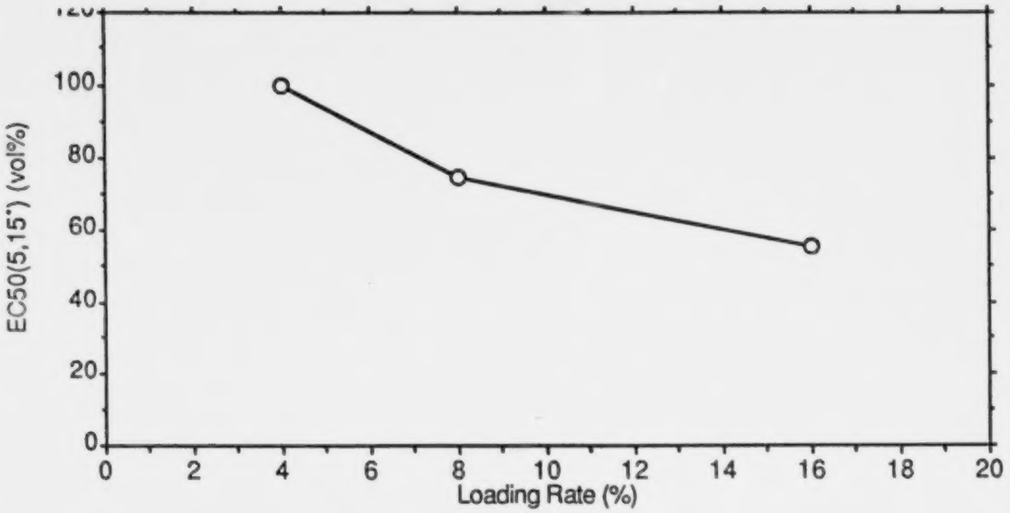

Figure 22. Toxicity of water soluble fraction measured by the Microtox assay for API separator sludge waste mixed with Kidman sandy loam soil for loading rate determination. EC50(5,15^o) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{o}C.

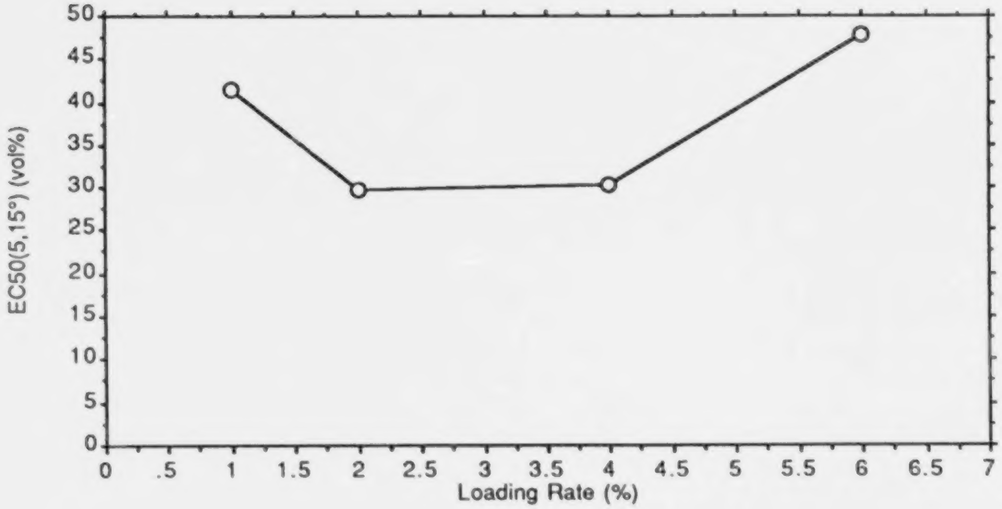

Figure 23. Toxicity of water soluble fraction measured by the Microtox assay for slop oil waste mixed with Durant clay loam soil for loading rate determination. EC50(5,15^o) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{o}C.

percent for the highest loading, 6 percent, was less toxic than the EC50 values for the lower loadings. As observed with the separator sludge waste, results from the Microtox system may be less helpful than with wood preserving wastes in determining waste loading rates for this particular soil and waste combination.

Figure 24 shows soil respiration results for slop oil:Durant clay loam mixtures. All loadings tested show an increase in CO_2 production over that of the soil control, with the highest loading, 6 percent, showing the greatest cumulative production of CO_2.

The following waste loading rates were selected for slop oil emulsion solids mixed with Durant clay loam soil based on Microtox and respiration results: 8 percent, 12 percent, and 14 percent waste wet weight/soil dry weight.

Figure 25 presents Microtox results for slop oil mixed with Kidman sandy loam soil. The results are similar to those obtained for mixtures of slop oil and Durant clay loam soil. The loading rates selected for slop oil:Kidman mixtures are lower than those for using Durant soil: 6 percent, 8 percent, and 12 percent waste wet weight/soil dry weight.

Summary of Loading Rates--

A summary of loading rates for all soil and waste types is presented in Table 48.

Acute Toxicity Comparison Study

The spectrum of microbes in the soil include organisms that are both procaryotic and eucaryotic and that have autotrophic, heterotrophic, and mixed autotrophic/heterotrophic metabolism. The autotrophs may be photosynthetic or chemoautotrophic, and the heterotrophs may be oligotrophic or prefer easily metabolizable substrates in rich abundance. Other organisms are strictly predatory. The types of compounds attacked and the rate of degradation of these compounds also varies widely among the soil microbes. The waste degradation process depends on the activities of a broad spectrum of soil microorganisms; however, the acute toxicity of a waste to soil microorganisms may inhibit degradation of the waste.

A comparative study of the sensitivity of Microtox, respiration, dehydrogenase, initial nitrification activity and soil plate counts to the pentachlorophenol (PCP) and slop oil wastes in the Kidman soil was performed to evaluate the response of commonly used bioassays to identical soil/waste mixtures and to evaluate the utility of a combination of these assays as indicators of soil microbial toxicity. Many other soil microbial activity assays exist that could be adapted to provide an indication of the acute toxicity.

The soil was acclimated for seven days, as described under "Preparation of Waste Soil Mixtures for Bioassays" and then treated with waste. The waste/soil mixture was incubated 24 ± 2 h at 20°C and then assayed. One-way

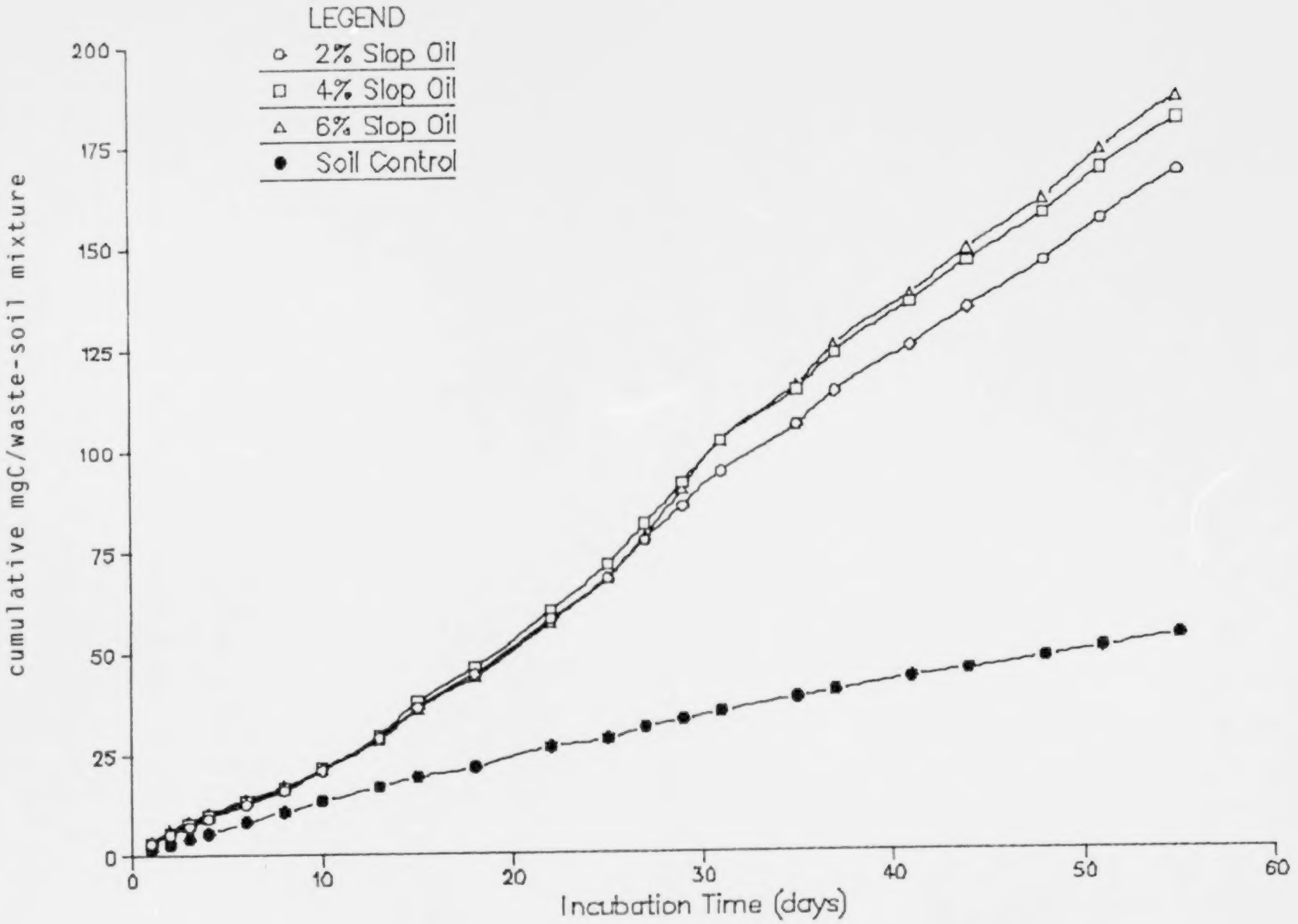

Figure 24. Soil respiration results for slop oil emulsion solids mixed with Durant clay loam soil.

analysis of variance and the least significant difference were used to identify significant differences among bioassay responses due to different waste loading rates.

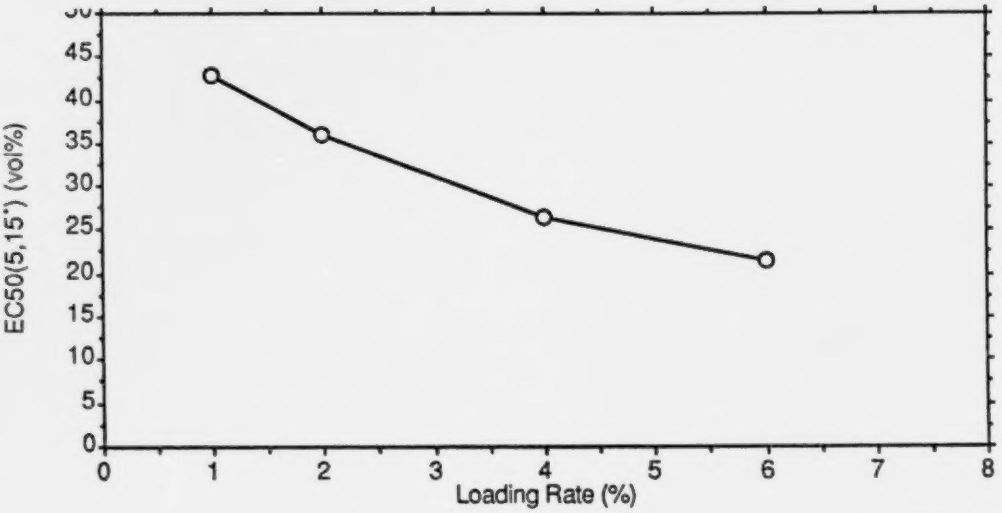

Figure 25. Toxicity of water soluble fraction measured by the Microtox assay for slop oil waste mixed with Kidman sandy loam soil for loading rate determination. EC50(5,15^{o}) denotes the conditions for the test, i.e., reading light output 5 minutes after sample addition at a temperature of 15^{o}C.

The responses of the assays to the PCP waste are illustrated in Figures 26 through 30. The Microtox assay was very sensitive to the aqueous extract of the soil-PCP waste mixtures, with less than 13 percent (vol:vol) of the extract of the 0.05 percent loading rate producing an EC_{50} (Figure 26). At the 0.5 percent loading rate the EC_{50} was about 3 percent (vol:vol) of the extract. These results indicate a high toxicity of the soil waste mixture to bacteria, even at loading rates of 0.05 percent or less.

Severe toxicity to initial nitrification activity was also observed at the 0.05 percent loading rate (Figure 27), where the average activity level was reduced to nearly 10 percent of the untreated control for both ammonium and nitrite ion oxidation rate. If nitrification activity is to be protected in this soil, application rates below 0.05 percent will be required. While the treatment site is being used and intensively managed, maintaining the nitrification process may not be necessary since nitrate fertilizers may be applied to meet nitrate demands if any arise. When the site is closed and returned to natural processes, however, reestablishment of nitrification processes will be important to nitrogen cycling processes in many environments. Perhaps the greatest value in the indication of nitrification toxicity lies in the implication that other specific biochemical processes may

TABLE 48. SOIL LOADING RATES FOR WASTES BASED ON MICROTOX AND SOIL RESPIRATION RESULTS

Waste	Loading Rates					
	Kidman Sandy Loam			Durant Clay Loam		
	Low	Medium	High	Low	Medium	High
	(% waste wet weight/soil dry weight)					
Creosote	0.4	0.7	1.0	0.7	1.0	1.3
Pentachlorophenol	0.075	0.15	0.3	0.3	0.5	0.7
API Separator Sludge	6	9	12	6	9	12
Slop Oil	6	8	12	8	12	14

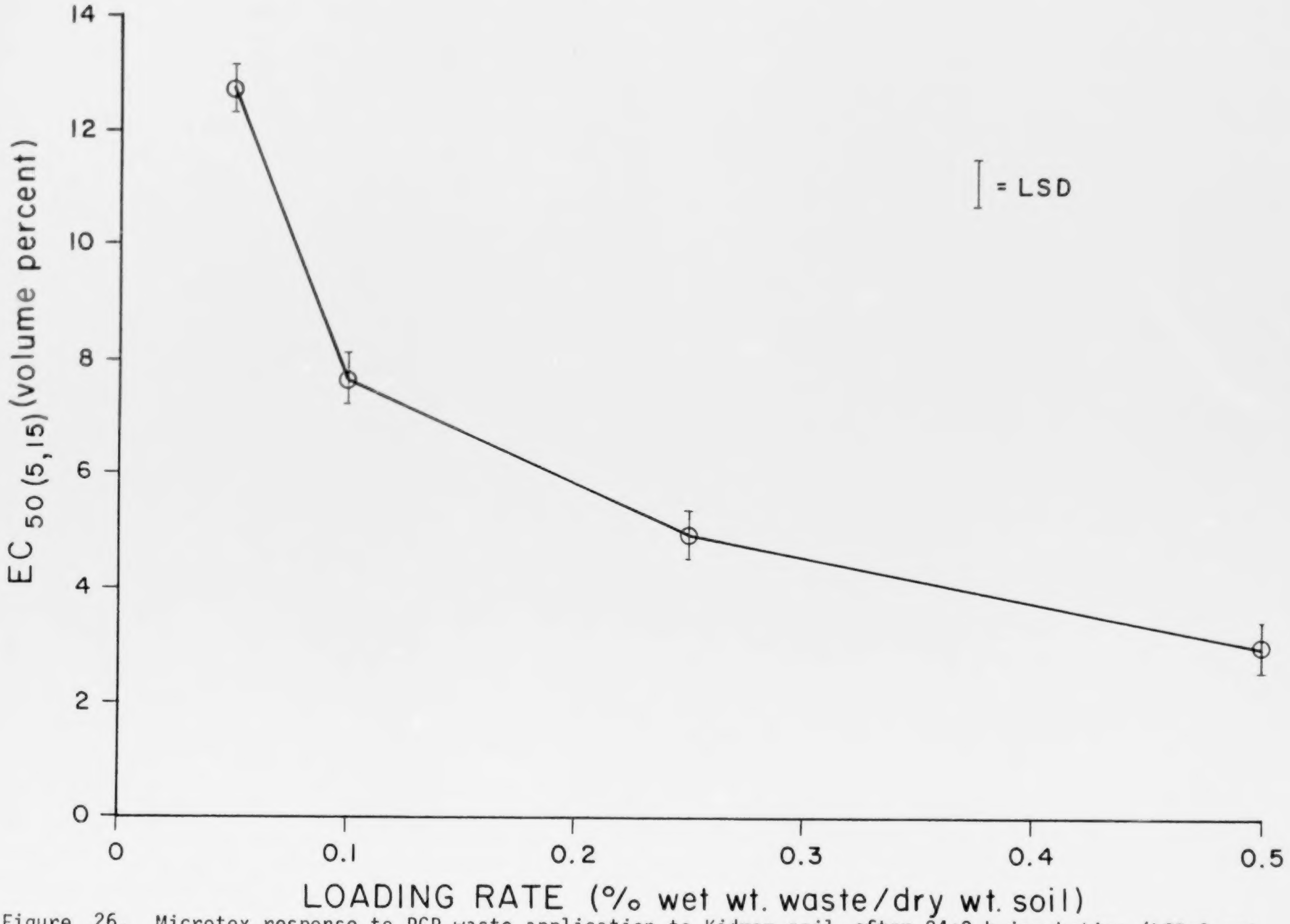

Figure 26. Microtox response to PCP waste application to Kidman soil after 24±2 h incubation (LSD=least significant difference).

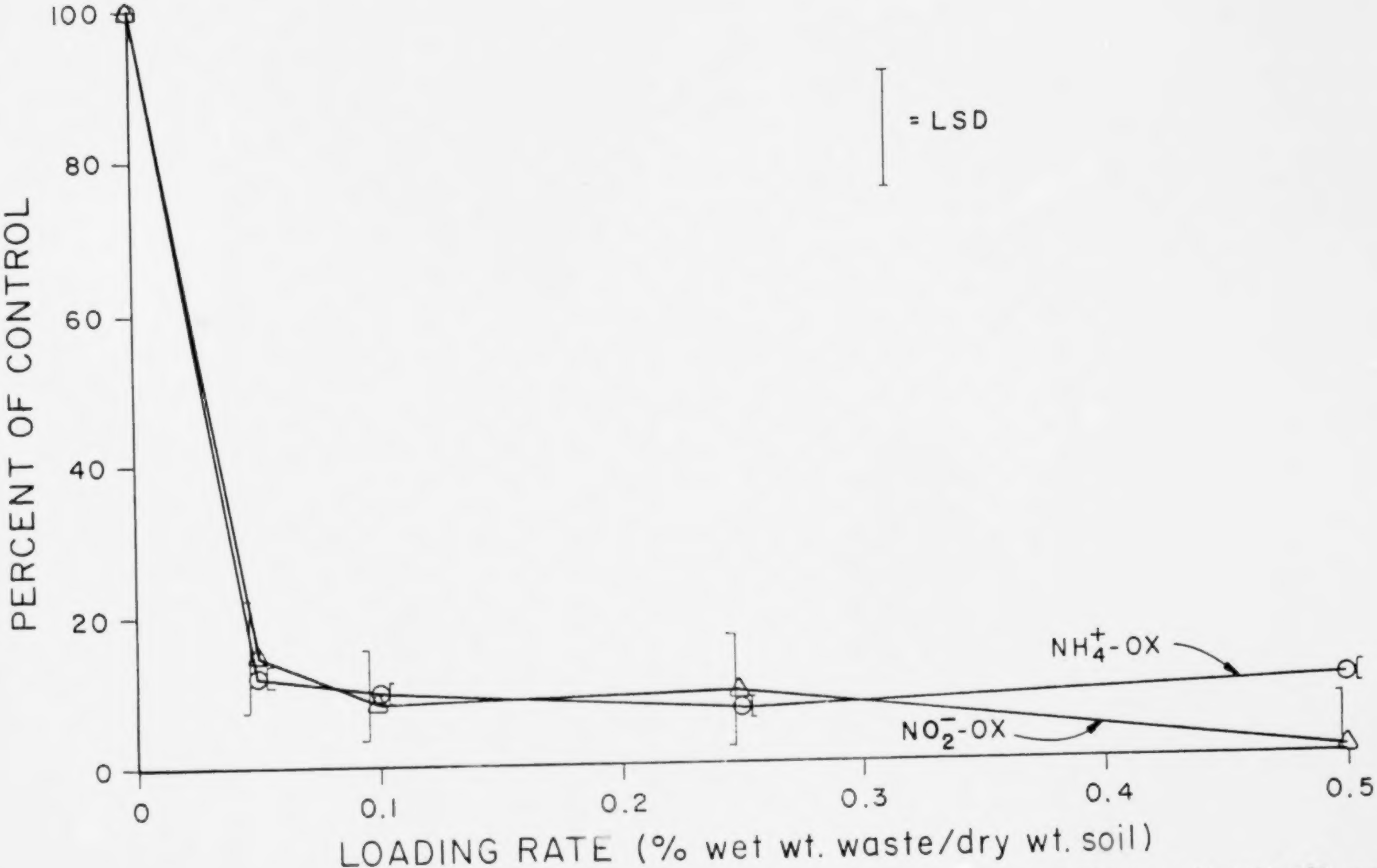

Figure 27. Initial ammonium and nitrite ion oxidation in response to treatment of Kidman soil with PCP waste after 24±2 h incubation (LSD= least significant difference).

also be impacted and that further investigation of biological effects is warranted.

Dehydrogenase activity also showed a toxic response to PCP waste (Figure 28), with similar response being shown in assays with and without glucose addition at all loading rates except at the 0.5 percent rate. The apparent stimulation of activity at the 0.5 percent rate in the assay, with glucose added, could reflect stimulation of organisms capable of degrading the hydrocarbon matrix of the PCP waste.

Respiration results (Figure 29) were highly variable, and no statistically significant difference ($p \leq 0.05$) could be found between the loading rates. However, the mean activity tended to increase with increasing loading rate, and then decreased slightly at the 0.5 percent rate. The lack of precision in the data make these results somewhat ambiguous, but no evidence of severe toxicity was shown with this assay.

The stimulation of activity in the hydrocarbon degrading portion of the microbial community that are resistant to PCP and other toxics in the waste may mask toxicity of the populations indicated by the Microtox, dehydrogenase, and nitrification assays. With this possibility in mind, a conservative approach would be to base loading rate decisions on the results of the Microtox, nitrification, and dehydrogenase assays. In this case, loading rates of 0.05 percent or less seem justified.

Viable counts of bacteria and fungi (Figure 30) do not reflect any toxicity of PCP waste at the loading rates tested. In fact, the fungal population increased significantly ($p \leq 0.05$) at the 0.25 percent loading rate. The slight increase in bacterial counts with loading rate is probably not significant.

Responses of the same battery of assays were also investigated with slop oil mixed with Kidman sandy loam soil. Respiration rates and counts of viable aerobic bacteria and fungi in the Kidman soil showed no significant toxicity of slop oil for application rates ranging from 2 to 14 percent. Microtox exhibited an EC50 at less than 10 percent of the aqueous extract of the 2 percent slop oil in Kidman soil (Figure 31), indicating considerable toxicity. Toxicity, as indicated by Microtox, increased significantly ($p \leq 0.05$) with an increase in slop oil loading from 2 to 6 percent, but changes in toxicity due to increases in loading to 10 and 14 percent did not cause significant increases in toxicity. The average Microtox EC50 increased at the 14 percent loading rate, and was not significantly different from the 2 percent loading rate.

Nitrification activities also showed significant toxicity of the slop oil waste (Figure 32). Ammonium ion oxidation was apparently more severely inhibited by the slop oil than nitrite ion oxidation. Nitrite ion oxidation was significantly less inhibited at the 10 and 14 percent loading rates than at the 2 and 6 percent loadings. The more extreme toxicity of slop oil to the ammonium oxidizing bacteria would inhibit the nitrification process, however.

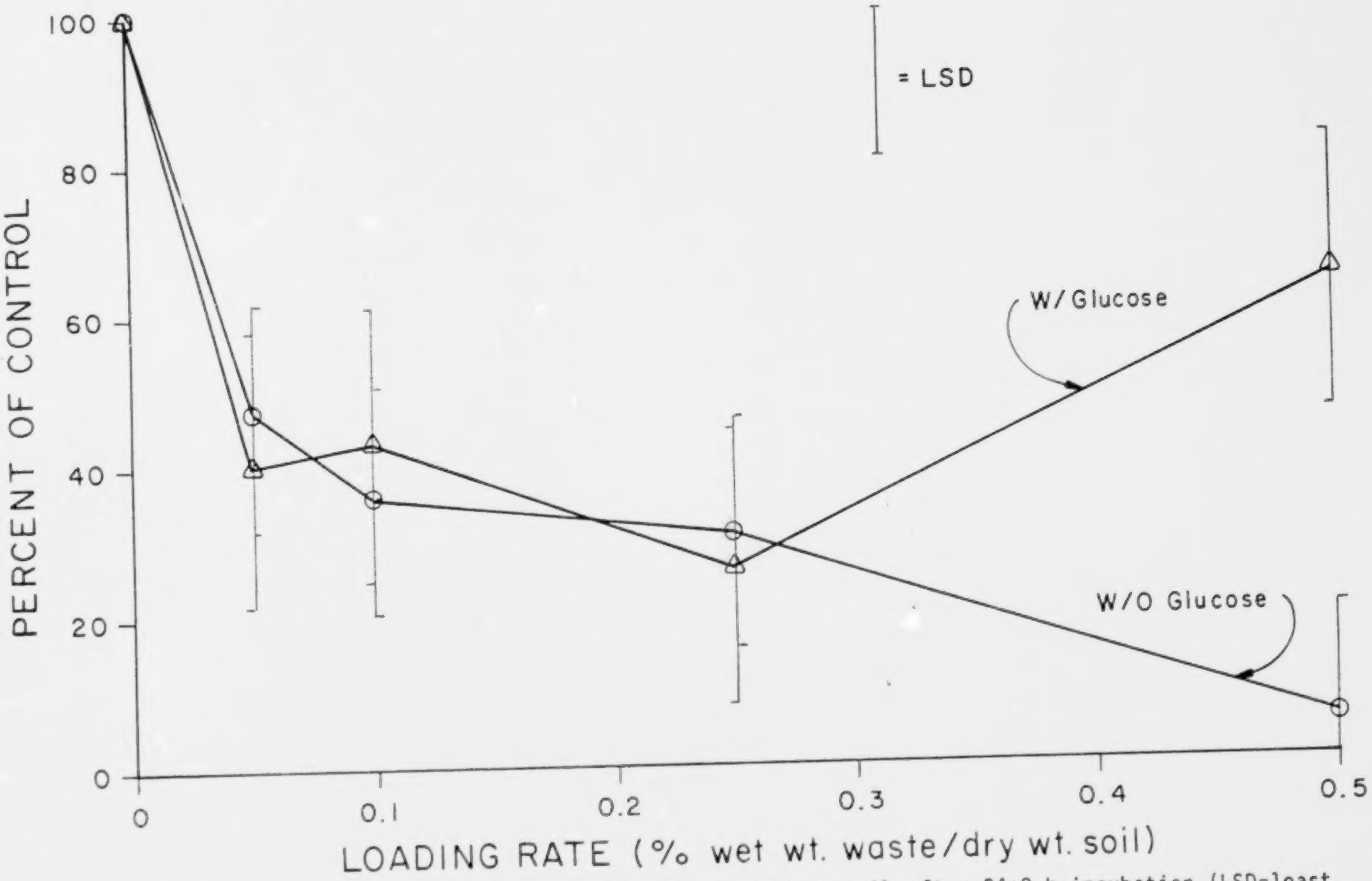

Figure 28. Dehydrogenase response to PCP application to Kidman soil after 24±2 h incubation (LSD=least significant difference).

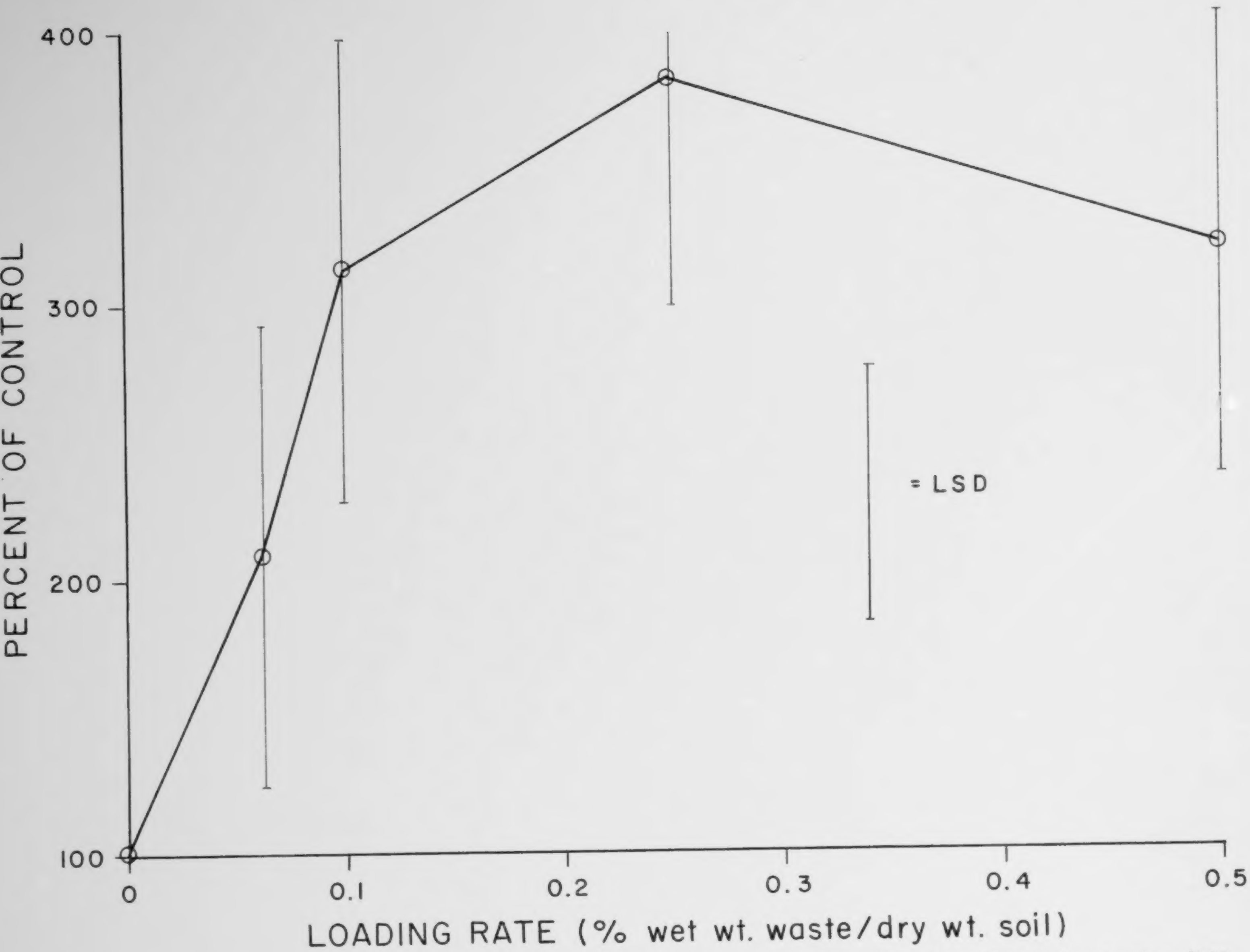

Figure 29. Respiration response to application of PCP waste to Kidman soil after 24±2 h incubation (LSD= least significant difference).

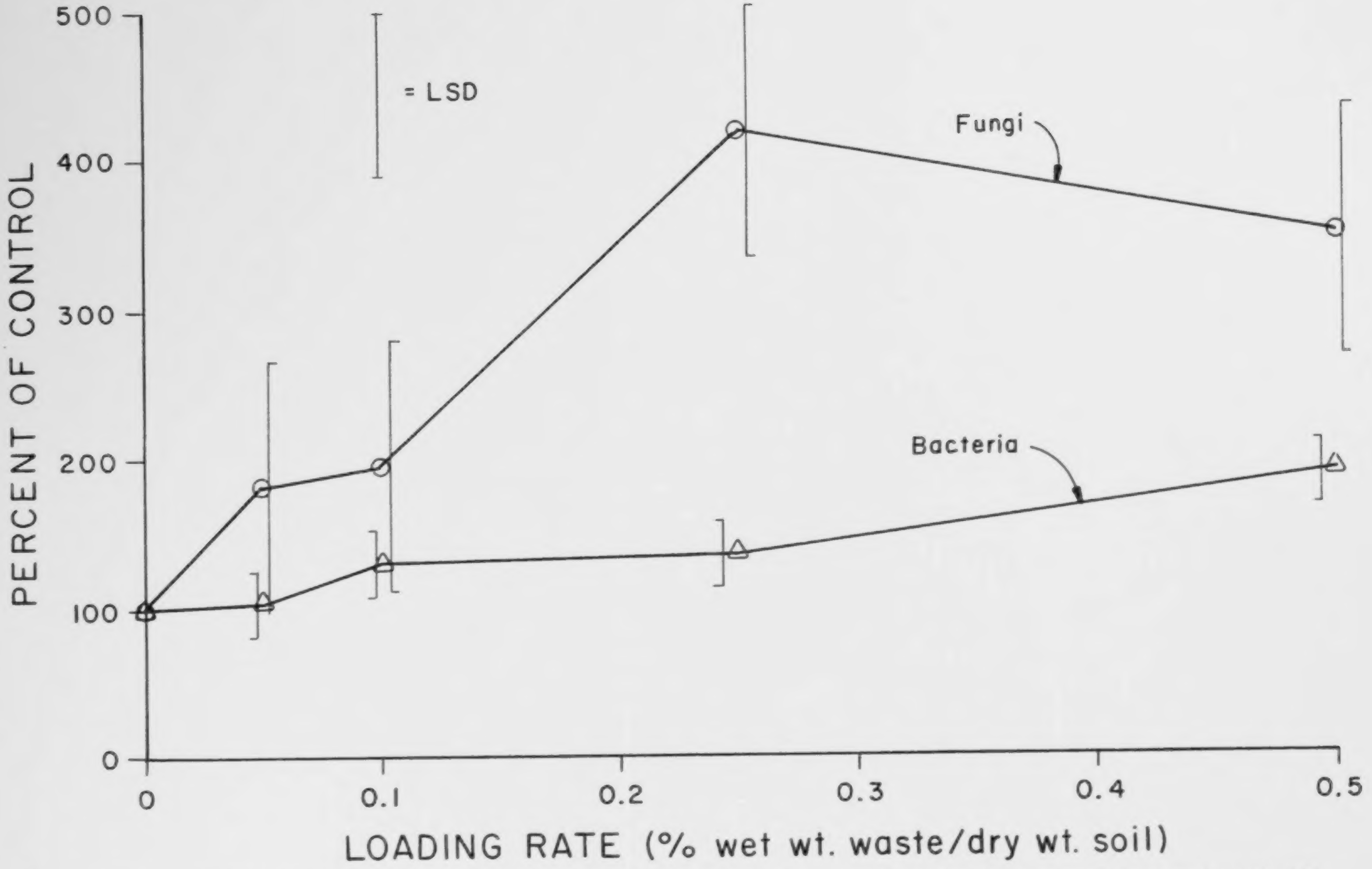

Figure 30. Viable aerobic heterotrophic bacteria and fungal propagules in Kidman soil treated with PCP waste after 24$\pm$2 h incubation (LSD=least significant difference).

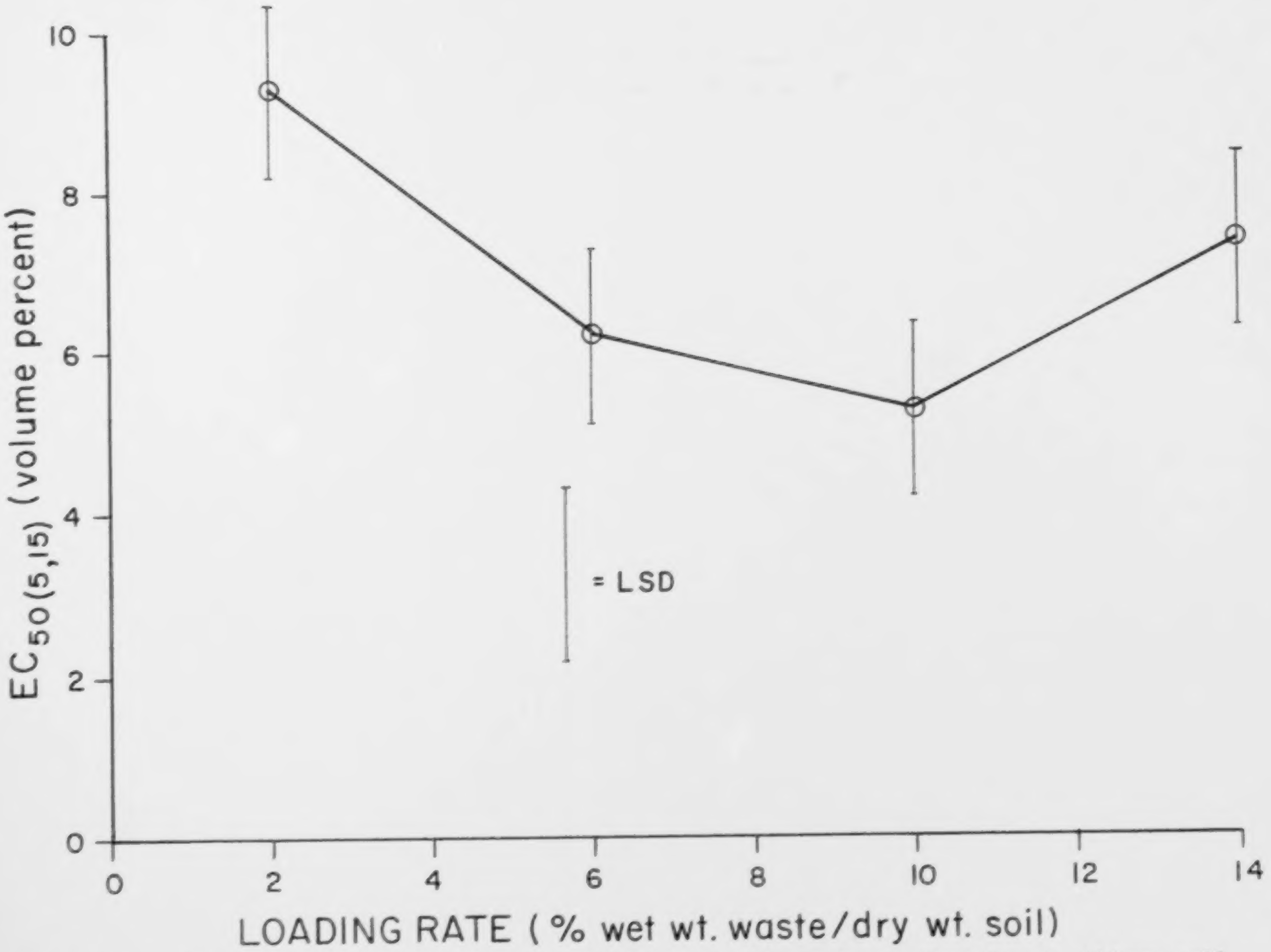

Figure 31. Microtox response to slop oil emulsion solids waste application to Kidman soil (LSD=least significant difference).

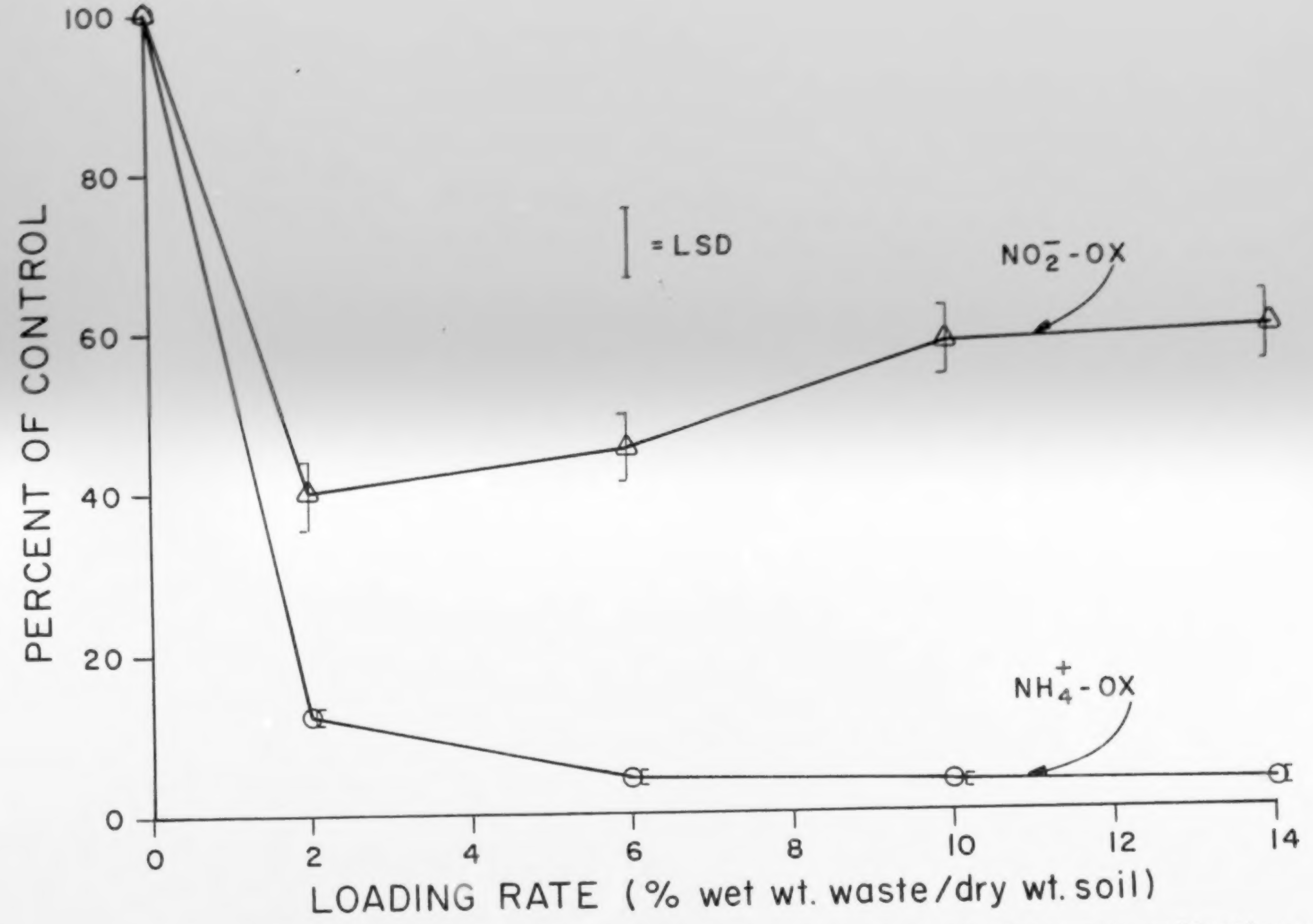

Figure 32. Initial ammonium and nitrite ion oxidation in response to treatment application of slop oil emulsion solids to Kidman soil (LSD=least significant difference).

Dehydrogenase activity, both with and without glucose addition, was inhibited 30 to 50 percent at the 2 percent loading rate (Figure 33). Dehydrogenase toxicity increased with increasing loading and activity was essentially nil at the 10 and 14 percent loadings in the assay without glucose addition. The assay with glucose continued to show some activity at the 14 percent loading rate.

These results illustrate the wide range of acute toxic response that is possible with various assays of soil microbial activity. In the Kidman soil, CO_2 evolution was highly variable and did not show toxic effects of either PCP or slop oil waste. Also, viable counts of bacteria and fungi were not responsive to the loadings of PCP and slop oil waste used in these experiments. The toxicity indicated by Microtox, nitrification, and dehydrogenase activities shows that significant groups of soil microbes are adversely affected by these wastes. These results show the importance of employing a battery of assays in determining the acute toxicity of wastes. Generally, the most confidence in determining the toxicity to the soil microbial community can be obtained when more than one assay indicates toxicity.

However, it was not possible to use the battery of assays consisting of Microtox, nitrification, and dehydrogenase to entirely predict the affect of demonstrated toxicity on waste degradation. More research using this specific battery of assays is needed to establish the relationship between acute toxicity indicators and observed waste decomposition rate and extent.

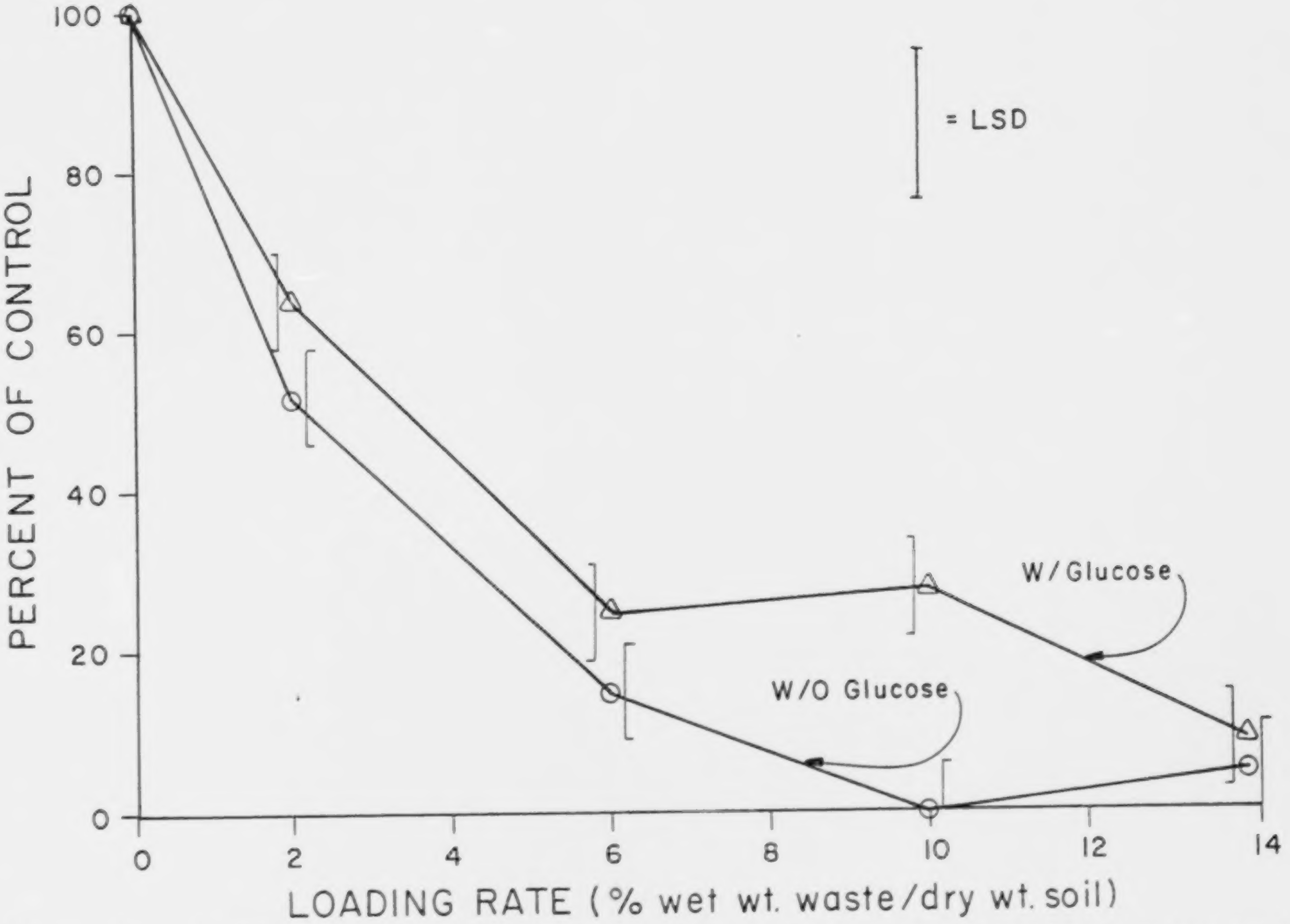

Figure 33. Dehydrogenase response to slop oil emulsion solids waste application to Kidman soil (LSD=least significant difference).

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